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H. EYRING, *Editor*
University of Utah

C. J. CHRISTENSEN, *Associate Editor*
University of Utah

H. S. JOHNSTON, *Associate Editor*
Stanford University

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PREFACE

Dr. G. K. Rollefson's passing came as a great shock to his many friends. Under his wise guidance, and with Dr. R. E. Powell's able assistance, the first six volumes of *Annual Reviews* have attained their present enviable position. Their wise selection of authors and topics continues on into volumes seven and eight. It will be the pleasant, although difficult, duty of the new editors and the editorial committee to continue in the spirit of this most auspicious beginning.

The present volume treats the same subjects as volume six except that the three chapters, (a) "Ion Exchange"; (b) "Combustion and Flames"; and (c) "High Temperature Chemistry" replace the chapters, (a) "Metal Chelate Compounds"; (b) "Electrode Processes and the Electrical Double Layer"; and (c) "Colloid Chemistry, Exclusive of High Polymers." Our plan is to continue to devote approximately three of the twenty-one chapters to subjects which require only occasional treatment.

The committee deeply appreciates the prompt and wholehearted cooperation that it continues to receive from the authors of the various chapters. In this it is joined by the army of users of this *Review*.

B.L.C.	H.S.J.
C.J.C.	G.E.K.
H.E.	J.G.K.
J.D.F.	F.A.L.

Faculty Recommendation

VIA COLLEGE BOOKSTORE NOV 4 1959

Gerhard K. Rollefson

1900-1955

With the unexpected death of Gerhard K. Rollefson, on November 15, 1955, the *Annual Review of Physical Chemistry* lost the editor who saw its first six volumes into print. Professor Rollefson brought to his editorial work the same careful judgment which characterized his scientific research. From the days when the *Annual Review of Physical Chemistry* was no more than an idea, he was firmly convinced of its worth to the scientific community. To no small extent, the stature this *Review* has gained is to be credited to his enthusiasm and capability as its editor.

To his colleagues at the University of California, where for 33 years he was a member of the faculty, to his colleagues in the field of photochemistry, in which he had worked for 26 years, and indeed to physical chemists generally, the Annual Reviews joins in expressing its sense of loss.

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VOLUME 8 (1957)

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CRYOGENICS[1]

By R. Berman, A. H. Cooke and R. W. Hill
Clarendon Laboratory, Oxford, England

This is the third article on Cryogenics to appear in this series. As in previous years, attention has been confined to a small number of topics. Those selected this year are the Third Law of Thermodynamics, the Liquid Helium Temperature Scale, and Antiferromagnetism.

THE THIRD LAW OF THERMODYNAMICS

After many years of controversy, there is now fairly general agreement on the definition and the usefulness of the third law. An accepted statement, due to Simon (1), is that "The contribution to the entropy due to each factor within the system which is in internal equilibrium, becomes zero at the absolute zero." In this review we shall limit ourselves to a discussion of the validity of this statement in the light of recent low temperature research.

The most common use of the third law is in the calculation of absolute entropies from calorimetric data. Suppose, for simplicity, that it is required to evaluate the entropy of a solid substance under zero external pressure at temperature T, and that the specific heat C_p of the substance has been measured down to some temperature T_1. The specific heat is extrapolated down to absolute zero using, say, the Debye formula, and the integral $\int_0^T C_p d(\ln T)$ evaluated; is this quantity then the absolute entropy of our substance? It is well known that in fact this procedure may give an incorrect value, and we may distinguish two ways in which it may fail. Firstly, there may be some degree of freedom which is still completely disordered at the lowest temperature of measurement, but which will tend to an ordered state at sufficiently low temperatures. Our specific heat measurements would give no hint of the existence of this disorder and our evaluation of the entropy would be incorrect, though there is clearly no violation of the third law. In fact, the error in the entropy is just an expression of our ignorance about the physical state of the substance. An example of this, which will be discussed in more detail later, is the entropy of the nuclear spin system.

The second way in which the procedure for evaluating the entropy may fail is when our system contains a degree of freedom which is "frozen in." By this we mean that when the system is cooled from a high temperature ($T > T_c$) where it is completely disordered to a low temperature ($T < T_c$) where an ordered state should occur, the transformation may not take place, due to the existence of some sort of potential barrier. The disorder corresponding to the high temperature is then said to be "frozen in" at the low temperature. Now the ability of a system to surmount a potential barrier

[1] The survey of the literature pertaining to this review was concluded in December, 1955.

depends on the Boltzmann factor exp $(-W/kT)$, where W is the barrier height; depending on the relative magnitudes of W and kT when $T \sim T_c$ the rate at which the ordered state is approached may be so fast that internal thermodynamic equilibrium is always attained, so slow that the system may be regarded as completely disordered under all circumstances, or of an intermediate magnitude.

In the first case there is no difficulty; the disorder is never frozen in and the entropy tends to zero at absolute zero. In the second case, however, the entropy contribution certainly does not go to zero. but this does not contravene the third law since this degree of freedom is not in internal thermodynamic equilibrium. Furthermore, we can still evaluate the absolute entropy, for as long as the system is completely disordered, the entropy can be calculated, though it cannot be found by thermal measurements. (The calorimetric and spectroscopic entropies will then differ by a fixed amount at all temperatures.) From the practical point of view, then, we may never assume that the calorimetric entropy is the true absolute entropy until we are sure that no frozen-in degrees of freedom exist. In monatomic and diatomic substances this presents little difficulty, but great care must be taken with polyatomic substances, as will be seen later.

Turning now to the third possibility, where the approach to equilibrium takes place slowly, but at a rate which must be considered finite for experimental purposes, it is evident that a more difficult situation exists. Since all ordering processes other than first order phase changes take place over a range of temperature, the system may only reach a state of incomplete order when cooled, the actual degree of order depending on the rate of cooling. In this case, the third law as stated is not broken, but it cannot be applied; we cannot make allowance for an entropy of disorder which is not uniquely defined by the external parameters of the system. In the range of temperatures where the relaxation time is essentially finite, all processes which involve a change in this degree of order are irreversible, and the second law of thermodynamics is inapplicable, though reversible changes will of course be possible at sufficiently low temperatures. These remarks are particularly applicable to glasses; a review of their thermodynamic properties has been given by Davies & Jones (2).

Having sketched the types of problem which attend the use of the third law, we will now discuss a number of topics which illustrate these remarks, choosing those which have necessarily to be investigated at low temperatures. We will then conclude with a discussion of the usefulness of the law in the form given here.

Nuclear Spins

The interaction between the nuclear spins of two atoms in a crystal lattice is so small that it becomes comparable with kT at temperatures of the order of 10^{-3} to 10^{-6}°K. It is therefore sufficient to regard the nuclear spin system as completely disordered at ordinary temperatures, with an

entropy of $k \ln (2I+1)$ per spin. This may be added to the calorimetric entropy to give the absolute entropy. Alternatively, we may ignore this contribution completely, since in any chemical or physical change the change of entropy will be the same whether the spin is included or not. This useful simplification is not exact except in the case of monatomic substances; in other cases its validity depends on our ability to factorize the rotation-nuclear spin partition function into a rotational and a nuclear spin part. This can be done to a very close approximation (see e.g. Folwer & Guggenheim (3)) provided that, at the temperatures concerned, a sufficiently large number of rotational states is occupied. The only substances which do not satisfy this criterion at normal temperatures are hydrogen and deuterium, for which a complete treatment must be used.

We have cited the nuclear spin system as one in which internal thermodynamic equilibrium can be achieved rapidly, so that its contribution to the entropy will tend to zero at absolute zero. For this to be true, it must be possible to transfer heat energy reasonably rapidly from the spin system to the lattice and vice versa. Experimental evidence on this point has only been obtained in recent years; from the success of nuclear alignment experiments it appears that the relaxation time for this transfer is not more than a few seconds in paramagnetic substances at temperatures down to 0.001°K., and is probably very much less. It is also believed that the rate can be reasonably large in metals, Rollin & Hatton (4), though for dielectric crystals free from paramagnetic impurity the spin disorder may well be frozen in. This would not, of course, invalidate either of the methods of treating the nuclear spin entropy just described.

Isotopic Mixtures

Most chemically pure substances are a mixture of isotopes, so that their entropies should properly include appropriate mixing terms. It is believed that this contribution to the entropy will not tend to zero at the absolute zero, but that a completely random distribution will be frozen in. Under these circumstances, we have the usual choice of calculating the entropy, or of ignoring it as irrelevant in any change which does not involve the separation of isotopes. It would, however, be against the spirit of the third law to dismiss the matter without enquiring whether an ordered distribution of isotopes would be energetically favourable at low temperatures. The most concrete calculations on this point are by Prigogine (5) and by Chester (6), both of whom predict some sort of phase separation at low temperatures; for hydrogen-deuterium a transformation temperature of about 2°K. is predicted, while for He^3-He^4 mixtures the temperature is given as 0.5°K. For heavier substances, the transformation temperature is even lower, and there is very little chance of the separation being observed experimentally. For hydrogen and helium, however, there is some possibility of the process taking place at an observable rate, but there is as yet no experimental information on this point.

Hindered Rotation

Turning now to some practical tests and applications of the third law, we consider first the case where the entropy can be calculated by the methods of statistical mechanics, the necessary physical parameters being obtained from spectroscopic measurements. A number of cases have been found where the spectroscopic and calorimetric entropies differ and it has sometimes been possible to show that the discrepancy is due to an incorrect method of calculating the spectroscopic entropy. This difficulty only arises in polyatomic molecules, and is due to the many additional degrees of freedom available.

An example of this is found in organic molecules containing one or more methyl groups. The group may rotate as a whole about a C-C bond, but if the rotation is treated as free, a discrepancy between entropies may be found, since the group rotates in a potential of the form $\frac{1}{2}V_0(1-\cos 3\phi)$ and therefore has a partition function quite different from that of a free rotator. The value of V_0 for a particular substance may not be known; if so, it may be possible to bring the calorimetric and spectroscopic entropies into agreement at one particular temperature by a suitable assumption about V_0 which allows the entropy to be calculated from the tables of Pitzer & Gwinn (7). This value may then be used to calculate the entropy at any other temperature. If agreement is found at all temperatures, the third law has been verified and the value of V_0 properly established. The theory of Pitzer and Gwinn is restricted to the case where the moments of inertia of the molecule for over-all rotation are not appreciably affected by internal rotation. Other substances cannot be treated in so general a manner; the important case of methyl alcohol has received a good deal of attention, the latest contribution being that of Ivash *et al.* (8).

A very elegant and satisfactory treatment of methylchloroform has recently been given by Pitzer & Hollenberg (9). In this investigation, V_0 was found directly from the infrared spectrum, so that the spectroscopic entropy could be calculated completely without reference to thermal data. The excellent agreement with the calorimetric entropy is very good evidence for the correctness of both the hindered rotation theory and of the third law.

Configurational Entropy

There is another group of substances which appear to disobey the third law, and in which the discrepancy has been traced to a frozen-in configurational disorder. A discrepancy of this type is apparent when comparison is made with entropies derived from reaction equilibrium data, since the configurational entropy depends on the symmetry properties of the molecules, which are changed in a chemical reaction. Probably the most famous case is that of water; the calorimetric entropy differing from that derived from reactions such as $Mg(OH)_2 = MgO + H_2O$ by 0.8 E.U. [Giauque & Archibald (10)]. The reason for this was given by Pauling (11), who showed the

discrepancy to be due to the entropy of disorder of the orientation of the hydrogen bonds. This disorder is frozen in at low temperatures and is consequently not included in the calorimetric entropy. Following the solution of this problem, experiments have been carried out on a number of other substances containing hydrogen, but no general rule has emerged. Sulphuric acid [Rubin & Giauque (12)] and some hydrated salts [Barieau & Giauque (13)] achieve an ordered state in this respect, while sodium sulphate decahydrate [Pitzer & Coulter (14)] does not.

Similar studies have been made for other simple molecules. Carbon monoxide, nitrous oxide and nitric oxide have long been known to resemble water in having a frozen-in configurational disorder. These molecules are composed of neighbouring atoms in the periodic table, so that the ends of the molecule are not very dissimilar; the tendency to configurational order should consequently be slight. In carbonyl sulphide, which forms a linear molecule whose ends are less similar, an ordered state is in fact achieved, though apparently rather slowly [Kemp & Giauque (15)]. On the other hand, nonlinear triatomic molecules such as carbonyl chloride [Giauque & Jones (16)] and sulphur dioxide [Giauque & Stephenson (17)] behave like ice. It therefore appears that disorders of this type may commonly be frozen in, and that only in favourable cases can ordering be achieved in the time scale of an experiment. The well-known anomaly in the specific heat and expansion coefficient of ammonium chloride is now known to be due to a process of this type [Lawson (18), Alpert (19)]; the alkali borohydrides show similar behaviour [Stephenson, Rice & Stockmayer (20)].

Hydrogen and Deuterium

When discussing the nuclear spin entropy we remarked that hydrogen and deuterium require a special treatment. It is necessary to take account of all the possible values of the total nuclear spin in the molecule (two for hydrogen and three for deuterium) and consider each configuration together with the rotational modes allowed to it by the exclusion principle. For hydrogen, the possible cases are $I=0$ and rotational quantum number $J=$even, which is called parahydrogen, and $I=1$ with odd J which is orthohydrogen. The equilibrium concentrations of the two species depend on the temperature; at room temperature and above it is given by the ratio of the nuclear weight factors $2I+1$ and is 75 per cent orthohydrogen, while at low temperatures pure parahydrogen is the stable form. In the absence of a catalyst, however, a mixture of any concentration is effectively stable for experimental purposes, not only in the gas phase but also in the liquid and solid.

The entropy of hydrogen at a given temperature and pressure evidently depends on the orthohydrogen concentration, and we will consider the usual case where this is 75 per cent. Then the entropy found by calorimetric experiments at temperatures down to 10°K, which is a few degrees below the triple point, will be less than that found from chemical equilibrium data since there are three degrees of freedom which have not been taken into account.

These are the nuclear spin entropy of $R \ln 3$, the rotational entropy which is also $R \ln 3$ since only the lowest ortho state $J=1$ is occupied at low temperatures, and an entropy of mixing of ortho and para molecules of $-R(\frac{3}{4} \ln \frac{3}{4}+\frac{1}{4} \ln \frac{1}{4})$. For pure parahydrogen with $I=0$ and $J=0$ there are no such terms, so that the calorimetric entropy has the absolute value [Johnston, Clark, Rifkin & Kerr (21)].

Measurements of the specific heat of solid hydrogen at temperatures from 2 to 10°K. show the existence of an anomaly which may be identified with the ordering of the rotations [Simon *et al.* (22, 23)]. More recent experiments have confirmed the earlier work, and by extending the range of measurement down to 0.3°K., have shown that the entropy of the anomaly per mole of orthohydrogen has just the value of $R \ln 3$, irrespective of the concentration actually studied [Hill & Ricketson (24) and Simon (25)]. The disorder of mixing of ortho and para molecules appears to remain frozen in at all temperatures, while the nuclear spin disorder will persist down to temperatures of the order of 10^{-3}°K.

In deuterium the position is slightly more complicated, as there are three possible values for the total nuclear spin. The treatment follows on the same lines as above, and Johnston *et al.* (26) have shown that there is an anomaly in the specific heat resembling that in hydrogen at the same concentration. The entropy of the anomaly has not been obtained very accurately, but there can be little doubt that the explanation is the same.

The Melting Curve of Solid Helium

The most direct demonstration of an entropy difference tending to zero is afforded by the melting curve of solid helium, a phase which exists only at pressures above about 25 atm. It has long been known that the slope dp/dT of the melting curve becomes very small at temperatures below 2°K. Then since the volume change remains finite, the entropy of melting must, by the Clausius-Clapeyron equation, tend to zero with dp/dT. Recently, the melting curve has been re-examined by Simon & Swenson (27), who have shown that at 1°K. the melting entropy is proportional to T^7, and has fallen to only 0.02 E.U./mole, compared with the value of 2 E.U./mole at 2°K., the latter being of the normal order of magnitude for melting entropies.

A similar effect can be demonstrated in solid nitrogen between two solid phases of presumably different crystal structure, both of which are stable at low temperatures. Experimentally, a phase transformation is observed at pressures of the order of 3400 atm.; dp/dT is very small and decreases apparently to zero at liquid helium temperatures, while the volume change remains finite [Swenson (28)].

In conclusion, we enquire whether the third law is in fact a useful law of thermodynamics in the restricted form which we have discussed; in particular we shall compare it with the second law in this respect. Both laws may be stated in either a positive or a negative manner, and in both cases

the negative statement is of universal application, while the positive statement must be used with discretion.

The negative statement of the second law may be taken as the Kelvin-Planck formulation: "It is impossible to construct an engine that, operating in a cycle, will produce no effect other than the extraction of heat from a reservoir and the performance of an equivalent amount of work." For the third law we have the statement that "it is impossible to reach absolute zero in a finite number of processes." Both of these laws are believed to be universally true, and neither has yet been derived from the other. However, the usefulness of the second law, to the physicist and chemist at least, does not lie in its condemnation of hypothetical machines, but in the fact that we may use it to demonstrate the existence of thermodynamic functions which depend only on the state of the system and not on its thermal history. But in order to take this fundamental step, we must restrict our attention to systems in which reversible changes can occur.

A similar state of affairs exists for the third law, for we find it necessary to restrict our attention to states of systems which are in internal thermodynamic equilibrium. This is a more stringent restriction than reversibility, for we must exclude frozen-in states although their presence does not introduce irreversibility with respect to any external parameter, at least at sufficiently low temperatures. States of this sort are not uncommon, and their non-existence cannot safely be assumed in any particular substance. For this reason, the use of the third law for predicting entropy values is somewhat limited. It is when the calorimetric and spectroscopic entropies are both known that the law is most useful, for we know that any discrepancy must be attributed to some degree of freedom which has either been frozen in or which has not come to an appreciable state of order at the lowest temperature of measurement. We may then investigate to see how the discrepancy arises, and thereby extend our knowledge of the solid state.

THE LIQUID HELIUM TEMPERATURE SCALE

I. Introduction

By the "Liquid Helium Temperature Scale" we mean the relation between the vapour pressure of liquid helium and the absolute, thermodynamic, temperature. An accurate knowledge of this relation is essential in low temperature physics, as measurement of the vapour pressure provides the chief method of determining temperatures in the liquid helium region. Other thermometers, for measuring very low temperatures within and outside the helium range, are frequently calibrated against the vapour pressure and their accuracy then also depends on the accuracy of the vapour pressure curve.

From the time of the first liquefaction of helium, in 1908, until about 1939 absolute temperatures were mainly established by using a helium gas thermometer. More recently other methods have been employed, of which the best known is the measurement of the susceptibility of paramagnetic salts.

The relation between vapour pressure and temperature is, of course, not arbitrary, but involves several properties of the liquid and vapour which can be measured as functions of the proposed temperature. The accuracy with which certain thermodynamic relations between these properties are satisfied is then a measure of the accuracy of the temperature scale.

Even if a temperature scale should later be found to be incorrect it is desirable that at any given time all authors should use the same scale. Any stated temperature will then have been derived from an easily ascertainable vapour pressure and can be corrected according to later, more accurate, scales.

There have been several accepted scales, designated by the year of their adoption, such as 1924, 1929, 1932 and 1937, and these are discussed in Keesom's book (29). Of these only the scale of 1932 [Keesom (30)] for temperatures below the λ-point (2.2°K.) was expressed in a form resembling the thermodynamic relation between vapour pressure and temperature. The first detailed calculation of a scale on a thermodynamic basis was made by Bleaney & Simon (31), also for temperatures below the λ-point.

The temperature scale which has been in use for the last seven years was agreed upon in Amsterdam in 1948 [van Dijk & Shoenberg (32)]. It is divided into three parts:

Below 1.6°K. the relation between helium vapour pressure and absolute temperature calculated by Bleaney and Simon was used

Between 1.6 and 4.3°K. the scale was based on gas thermometer measurements by Schmidt & Keesom (33)

Between 4.3 and 5.2°K. (the critical temperature) a vapour pressure formula was used which fitted the few gas thermometer measurements of Kamerlingh Onnes & Weber (34).

Even before the 1948 scale was adopted there was reason to believe that it might be slightly in error. Since then, with the great expansion of low temperature physics, further evidence of errors in the scale has arisen from several kinds of measurement which can now be made with high precision. This evidence will be outlined below and afterwards the present proposals for a temperature scale discussed.

II. Evidence of Errors in the 1948 Scale

(*a*) *Gas thermometry.*—For a real gas the relation between pressure and volume can be expressed by an equation such as

$$PV = A(1 + B/V + C/V^2 + \cdots) \qquad 1.$$

where the virial coefficients A, B, $C \cdots$ are functions of the temperature and are determined by measurements of isotherms. The absolute temperature can be derived from such measurements since $T = A/R$.

In normal gas thermometry the pressure is usually made low enough so that the departures from ideality can be calculated with sufficient accuracy from existing isotherm measurements. On the other hand, if the pressure is

too low large corrections have to be applied for the thermo-molecular pressure difference in the measuring system. Some compromise is therefore necessary in choosing the pressure and the accuracy is limited.

Kistemaker & Keesom (35) determined five isotherms between 1.8° and 2.7°K. and Kistemaker (36) made gas thermometer measurements from 1.3° to the λ-point. From these Kistemaker derived a scale for temperatures below the λ-point which, by thermodynamic reasoning (37), he was able to show was more self-consistent than the 1937 scale. The 1937 scale for temperatures between 1.6° and 4.3°K. was adopted as the 1948 scale, nevertheless, as it was felt that further confirmation of Kistemaker's results was necessary.

Keller (38) has recently measured five isotherms of He^4 between 2.15° and 3.96°K. and finds that up to the pressures used they can be represented by the first two terms of equation 1. The temperatures derived from the values of A differed from the 1948 scale in a way similar to that deduced by other methods. He has also (39) measured five isotherms of He^3 between 1.5° and 3.8°K. The three higher ones are considered more accurate and the temperatures derived from them show similar deviations from the 1948 scale.

Berman & Swenson (40) made gas thermometer measurements between the boiling point (4.2°K.) and the critical temperature (5.2°K.), calibrating the thermometer against the vapour pressure of liquid hydrogen. Using the same hydrogen vapour pressure scale as had been used by Schmidt & Keesom (41) in their determinations of the helium boiling point, both the boiling point and the critical temperature were confirmed very closely. At intermediate temperatures there were considerable departures from the 1948 scale, the maximum being about 0.02° at 4.9°K.

(*b*) *Magnetic susceptibility.*—For a paramagnetic salt which obeys the Curie-Weiss law the susceptibility is given by

$$\chi = \frac{C}{T + \Delta} \qquad 2.$$

where C and Δ are constants. The constants can be determined by measurements at two temperatures and the salt can then be used to examine the consistency of the temperature scale. Extensive measurements carried out in Leiden since 1949 have confirmed Kistemaker's results. From his experiments it appeared that the scale was correct at 1.5° and there is considerable evidence that it was also correct at 4.2°K. Van Dijk & Durieux (42) give a table of the difference between their magnetic temperature scale and the 1948 scale when the constants of equation 2 are such that these two temperatures are unchanged.

Similar experiments have been carried out by Erickson & Roberts (43) and by Ambler & Hudson (44).

(*c*) *Specific heat of simple solids.*—Clement (45) pointed out that some very small anomalies (variation of Debye θ with temperature) in specific

heats at liquid helium temperatures which had been measured before the 1948 scale was adopted, could be attributed to errors in the temperature scale in use at the time of the measurements. He further showed that the apparent rise in the Debye characteristic temperature of KCl below 2°K., according to the later measurements of Keesom & Pearlman (46), almost disappeared if the temperature scale were corrected according to Kistemaker's suggestions. Keesom & Pearlman (47) have re-evaluated their own data on silver (48) in a similar way and this also removes an apparent anomaly. Corak *et al.* (49) have recently made very accurate measurements of the specific heats of copper, silver and gold between 1° and 5°K. At these temperatures ($T < \theta/50$) the specific heat, c, of such a metal should conform to the expression

$$c = aT + bT^3 \qquad 3.$$

where the first term is the electronic contribution and the second is the lattice specific heat. It was found that if the 1948 scale were used to calibrate the thermometers, then there were slight deviations from equation 3 which were similar for each metal. If it is assumed that equation 3 is correct it is possible to derive a temperature scale from the specific heat measurements. The determination of the absolute temperature from such measurements is not quite straightforward, as it does not merely involve changing the temperature corresponding to each measurement in such a way as to give the correct variation of the specific heat. If T_e is the experimental temperature determined by reference to the helium vapour pressure and T is the absolute temperature, then the true heat capacity is related to the heat input, Q, by the relation

$$c = \frac{dQ}{dT_e}\frac{dT_e}{dT}.$$

The value of the specific heat itself therefore depends on the temperature scale used. It was, in fact, necessary to assume the correctness of three points on the vapour-pressure curve in order to derive a new scale and these were taken to be the normal boiling point on the 1948 scale and the temperatures of 1.6 and 2.9°K., determined by magnetic susceptibility measurements. The resulting temperature scale is in good agreement with that derived by other methods.

(*d*) *Carbon resistance thermometers.*—Carbon resistors are frequently used as thermometers in the liquid helium range. The variation of their electrical resistance with temperature does not obey any simple law, but the relation can be expected to be a smooth function. Worley *et al.* (50) calibrated several carbon resistors between 1.8 and 4.2°K. against the vapour pressure of liquid helium and derived an empirical formula which would fit these data and also join on to the resistance measured at the triple point of hydrogen. They found that the resistance deduced from this relation did not agree with direct measurements made between 4.2° and 4.8°K., if the temperature was derived from the measured vapour pressure according to

the 1948 scale. It was concluded that the 1948 scale was in error above 4.2°K. and that the error at 4.8° was 0.06°.

Clement *et al.* (51) have examined in some detail the calibration of carbon resistors. They find that a constant a can be found such that the parameter b, defined by the equation

$$b = a \log R - (\log R/T)^{1/2}$$

is very nearly independent of temperature; R is the electrical resistance. Although there is no theoretical expression for the variation of b with temperature it is reasonable that b should be a smooth function of T or of log R. Using the 1948 scale the values of b have a peak at the λ-point of liquid helium (2.2°K.), and this suggested a re-examination of the 1948 scale. Clement *et al.* collected together the various corrections to the scale which had been proposed by other authors and recalculated values of their parameter b. This showed a much smoother variation with temperature, and it was reasonable to draw a smooth curve through the b values. This curve could then be used to recalculate the temperature scale. This must of course be similar to the scales which have been used to derive the values of b, but the advantage of the carbon resistor measurements is that if enough calibration temperatures are known from other measurements it is easy to interpolate intermediate temperatures with a high relative accuracy.

III. The 1955 Temperature Scale

The adoption of a new temperature scale was discussed at the International Conference on Low Temperature Physics held in Paris in the summer of 1955. It was agreed that the new scale, with temperatures denoted by T_{55}, should be between 0.9° and 4.25°K., the one calculated on a thermodynamic basis by van Dijk & Durieux (42). For higher temperatures the scale would be based on the gas thermometer measurements of Berman and Swenson.

It was pointed out that for the conversion of measured vapour pressures to absolute temperatures a scale differing slightly from the calculated scale might be more appropriate. Such an experimental scale is discussed in section IV.

(*a*) *The scale below 4.25°K.*—The calculation is made by equating the Gibbs functions of the liquid and of the saturated vapour. This leads to the equation for the vapour pressure, p:

$$\ln p = i_0 - L_0/RT + 5/2 \ln T - 1/RT \int_0^T S_l dT + 1/RT \int_0^T v_l (dp/dT)_{sat} dT - \phi(v_g) \quad 4.$$

where i_0 is the chemical constant

L_0 is the latent heat of evaporation at 0°K.

S_l is the entropy of the liquid and v_l its volume and

$\phi(v_g)$ is the correction to the Gibbs function of the vapour to take account of departures from ideality.

The first three terms on the right hand side of equation 4 are the main ones, and of these i_0 and $5/2 \ln T$ can be calculated accurately. L_0 has to be calculated from other measurements and two methods have been used for this. The relevant equations are:

$$L_0' = L_{exp} - 5/2RT + \int_0^T C_l dT - RT/v_g(B - TdB/dT) + \int_0^T v_l(dp/dT)_{sat}dT \quad 5.$$

$$L_0'' = RT\{\ln (T^{5/2}/p) + i_0\} - RT\phi(v_g) - \int_0^T S_l dT + \int_0^T v_l(dp/dT)_{sat}dT. \quad 6.$$

L_{exp} is the experimentally determined latent heat at temperature T and C_l is the specific heat of the liquid.

The last three terms in both these equations are corrections which become smaller the lower the temperature and van Dijk and Durieux used the average of the values of L_0 calculated from data at temperatures between 1.5° and 2.5°K. This is 59.50 joules/mole, and differs from the value calculated by Bleaney and Simon by only a few tenths of one per cent.

The three correction terms in equation 4 can be calculated with sufficient accuracy for temperatures below 2.2°K., and for higher temperatures the main uncertainty arises from the term $\int S_l dT$. The entropy is derived from the specific heat, C_l, and it could be seen that C_l and S_l were in error since values calculated for L_0 above 2.5°K. from equations 5 and 6 differed: this difference increased with temperature, corresponding to the different signs of the terms in the two equations. C_l was therefore calculated in the following way:

Equation 5 can be rewritten to obtain

$$C_l = d/dT\left\{L_0' + 5/2RT + RT/v_g(B - TdB/dT) - \int_0^T v_l(dp/dT)_{sat}dT - L_{exp}\right\}.$$

L_0' was again taken as 59.50 joules/mole and L_{exp} was obtained from the data of Dana & Kamerlingh Onnes (52). From the values of C_l calculated in this way S_l was derived and substituted in equation 4.

The term $\int_0^T v_l(dp/dT)_{sat}dT$ is small and was calculated from the data of Kamerlingh Onnes & Boks (53).

If the equation of state of the vapour can be represented by equation 1 without using any terms beyond B/V, then to a sufficiently close approximation $\phi(v_g) = 2B/v_g - \ln (pv_g/RT)$. $\phi(v_g)$ was calculated by using the values of B given by Kilpatrick *et al.* (54) and the results are in very close agreement with earlier calculations by Erickson and Roberts who used older virial coefficient data.

A table was prepared for the Paris conference giving the vapour pressure (in mm. Hg at 0°C.) as a function of temperature at intervals of 0.01°, and this has since been expanded to give the pressure at intervals of 0.001°.

(*b*) *The scale above 4.25°K.*—The scale determined by Berman and Swenson is based on a normal hydrogen boiling point of 20.38°K., as found by Keesom *et al.* (55). The helium boiling point determined by Schmidt and

Keesom (4.216°K. for a pressure of 76 cm. Hg at 0°C.) was also based on this value of the hydrogen boiling point and the new measurements confirm this within the experimental accuracy (.002°). This also agrees very well with the value of 4.215°K. calculated by van Dijk and Durieux.

Moessen *et al.* (56) have discussed the probable value for the hydrogen boiling point and suggest that the value 20.37 ±0.01°K. should be used at present. This would lower the helium boiling point determined by a gas thermometer by 0.002°, but it would still be equal to the calculated value within the experimental error.

Berman and Swenson expressed their results by the formula:

$$\log p = 0.97864 - 2.77708/T + 2.5 \log T \qquad 7.$$

where the pressure is in cm. Hg at 20°C. The agreement with the van Dijk and Durieux scale can be seen not only from the values of the boiling point, but from the slopes of the vapour pressure curves where they overlap. At 4.2° the first and second derivatives are as follows:

$\frac{dp}{dT}$ v.D. and D. 71.9, B and S. 71.65 cm. Hg at 0°C/°

$\frac{d^2p}{dT^2}$ · · · · · 50.5, · · · · 45.1 cm./°/°.

Equation 7 has no theoretical basis, but it is of the form which is often found to fit vapour pressure data quite well even when the correction terms are large. It is possible that an even better overlap in the two temperature scales could be obtained by a small change in the constants of the Berman and Swenson formula or by giving it a slightly different form, still consistent with the experimental results. However, the gas thermometer measurements are not sufficiently accurate to warrant the derivation of a different formula by consideration of them alone.

The critical point was not redetermined, but the critical pressure of 171.8 cm. Hg (at 0°C.) which Kamerlingh Onnes and Weber reported corresponds, on the new scale, to a temperature of 5.206°K.

IV. The Experimental Temperature Scale

Systematic deviations have been found in experiments both in Leiden and in the U. S. from the van Dijk-Durieux scale. These deviations are of the order of a few millidegrees and appear to be connected with the experimental determination of vapour pressure, rather than with uncertainties in the absolute temperature. This was recognised at the Paris Conference by the proposal that for practical purposes one could use a scale based on direct measurements. Clement has developed such a scale from the various U. S. experiments (38, 39, 40, 43, 44, 49, 51) and has prescribed the two possible measuring conditions for determining the vapour pressure:

(a) If the pressure is measured over a bath of liquid helium, a heat source must be provided at the bottom of the bath to maintain a flow of bubbles

up through the liquid. Above the λ-point there must be added to the directly read pressure a pressure equal to that exerted by the liquid helium column above the object whose temperature is to be determined.

(b) If the pressure is measured over a small amount of liquid condensed in a bulb, certain precautions have to be taken in shielding the pressure transmitting line.

It is suggested that temperatures deduced from this scale should be denoted by the symbol T_{55E}. The scale has been tabulated by Clement (57) in the form of temperature as a function of pressure, which is more convenient for most experimental purposes than the reverse tabulation of the van Dijk-Durieux scale. The pressure is expressed in terms of mm. Hg at 20°C., which is near to the temperatures at which measurements are usually made.

V. Comparison of the 1948, 1955 and 1955E Scales

Both the new scales will be in the possession of most laboratories where experiments are made at liquid helium temperatures, so that only a short table is given here to show the difference between the 1948 scale and the two new scales. It is assumed that a vapour pressure has been read which according to the 1955 scale corresponds to the temperature shown in the first column. This pressure is given in the second and third columns in terms of mm. Hg at 0°C. and 20°C. The fourth column gives the difference between the temperature in column 1 and the temperature which would have been given by the 1948 scale, and the fifth column gives the deviation from the new experimental scale.

TABLE I

Comparison of 1948, 1955, and 1955E Scales

	T_{55}	$P_{mm.}$ Hg at 0°C.	$P_{mm.}$ Hg at 20°C.	$T_{48}-T_{55}$	$T_{55E}-T_{55}$
	1.000	0.1217	0.1221	0.001	0.003
	1.500	3.634	3.647	0.003	0.003
	2.000	23.930	24.017	0.008	0.003
λ-point	2.170	37.864	38.002	0.012	0.003
	2.500	77.793	78.077	0.008	0.002
	3.000	182.23	182.89	0.006	−0.001
	3.500	355.16	356.46	0.007	−0.002
	4.000	615.45	617.70	0.003	−0.002
boiling point	4.215	760.0	762.77	0.000	−0.001
	T_{58}	$P_{mm.}$ Hg at 0°C.	$P_{mm.}$ Hg at 20°C.	$T_{48}-T_{58}$	$T_{55E}-T_{58}$
	4.500	983.9	987.5	0.005	−0.001
	5.000	1476	1481	0.016	−0.007
critical temperature	5.206	1718	1724	−0.001	−0.012

van Dijk and Durieux have not yet published their version of the scale above the normal boiling point,[2] so that in the table T_{55} is replaced by T_{BS}, the temperature deduced from the Berman and Swenson scale, given by equation 7.

VI. Summary

It has been evident for some time that the helium temperature scale adopted in 1948 is in error, especially in the neighbourhood of the λ-point. Although the absolute magnitude of the errors is small, they are sufficient to show up in many experiments and give rise to apparent anomalies in the temperature variation of various properties of matter. Van Dijk and Durieux have calculated a relation between helium vapour pressure and absolute temperature such that the properties of liquid helium and its vapour are thermodynamically consistent. This scale has been adopted and temperatures derived by it from the vapour pressure are denoted by T_{55}.

There are certain difficulties in making unambiguous determinations of vapour pressure at these temperatures, and it is recognised that there may be small differences between a measured vapour pressure and the true vapour pressure which is appropriate to the use of the 1955 temperature scale. Clement has drawn up a scale which represents the relation between vapour pressure, measured in certain specified ways, and the absolute temperature. This scale differs from the van Dijk-Durieux scale by not more than three millidegrees and may be used for practical purposes.

The present position is, of course, somewhat unsatisfactory but a possible source of the existing uncertainties is recognised. Although it is to be expected that future work will still further reduce the possible errors in temperature measurement, either of the 1955 scales is a great improvement on the 1948 scale. It was therefore considered appropriate to include an outline of their genesis in this review.

ANTIFERROMAGNETISM

Though antiferromagnetism has now been studied for more than twenty years, there has recently been a quickening of interest in the subject, mainly from the development of new methods of investigation which give very detailed information about the antiferromagnetic state. As comprehensive reviews have recently been given by Lidiard (58) and by Nagamiya, Yosida & Kubo (59), this report is confined to a brief survey of the present position and a consideration of the most recent work.

The basic idea was propounded by Néel. In certain paramagnetic substances, exchange interaction tends to align neighbouring magnetic atoms or ions with their magnetic moments antiparallel. The properties of a number of these substances can be accounted for by the hypothesis that below a cer-

[2] This has now been published and is available from the Director, Kamerlingh Onnes Laboratorium, Leiden, Holland. It shows that the difference of 0.001° between T_{55} and T_{BS} at the boiling point has been maintained up to the critical temperature.

tain critical temperature the magnetic atoms form two interpenetrating lattices, all the atoms on one lattice tending to be aligned parallel to one another, but antiparallel to the atoms of the other lattice. Near absolute zero the alignment of the two opposing systems is complete. Néel, van Vleck and others developed the theory of the macroscopic magnetic properties of such substances. A simple case arises if the magnetic atoms form, say, a body-centered cubic lattice, which may be considered as two interpenetrating simple cubic sub-lattices, with the nearest neighbours of an atom on one sub-lattice all lying on the other. If exchange interaction is appreciable only between nearest neghbours, it can be shown that at high temperatures the magnetic susceptibility follows a Curie-Weiss law, $\chi = C/(T-\theta)$, with a negative value of θ. Antiferromagnetic ordering sets in at a temperature $T_c = -\theta$. (We must postulate some departure from cubic symmetry, in order to provide the anisotropy which determines the axis of antiferromagnetic alignment.) In the neighbourhood of T_c there is a specific heat anomaly of the co-operative type. Below T_c the magnetic susceptibility perpendicular to the axis of alignment is independent of temperature, while parallel to the axis the susceptibility falls with temperature, reaching zero at absolute zero. When we consider other crystal structures, and remove the restriction that exchange is appreciable only between nearest neighbours, the antiferromagnetic ordering is less simple, but the general picture is similar. Magnetic and thermal investigations have shown that the behaviour of a number of substances conforms closely to that predicted. The fluorides MnF_2, FeF_2, and CoF_2, studied by Stout and his collaborators, provide an excellent example [Stout & Adams (60); Griffel & Stout (61); Stout & Matarrese (62); Stout & Catalano (63)]. There are however other cases in which it is difficult to decide from the macroscopic properties whether antiferromagnetism occurs at all.

Neutron diffraction studies have given conclusive evidence of antiferromagnetic ordering in a number of substances. For atoms or ions having an electronic magnetic moment the magnetic scattering of neutrons is comparable in intensity with the nuclear scattering. Antiferromagnetic ordering therefore shows up in neutron diffraction experiments by the appearance of extra lines corresponding to the spacing of the magnetic sub-lattices (for example, in the simple case above, lines corresponding to twice the spacing of the 100 planes). The first application of this new method was made by Shull & Smart (64) to MnO and Fe_2O_3. Since then observations have been made on MnF_2, FeF_2, CoF_2, NiF_2 by Erickson (65), on Cr and α-Mn by Shull & Wilkinson (66), on V_3Si, Cr_3Si and Mo_3Si by Koehler & Wollan (67), on CuO and Cr_2O_3 by Brockhouse (68), on $MnCl_2$ by Wilkinson & Shull (66) and on a number of perovskite type compounds $(1-x)$La, xCa MnO_3 by Wolan & Koehler (69).

Recently much attention has been given to substances having their antiferromagnetic transition at a low temperature. It will be clear that the temperature T_c gives a rough measure of the interaction forces. If this transition temperature is low, these forces are comparatively weak, and the

possibility arises of studying the behaviour of the substance in a field strong enough to disturb the antiferromagnetic alignment. Consider for example an antiferromagnetic at a temperature well below T_c. The alignment of the two sub-lattices is then practically complete. A field perpendicular to the axis of alignment produces a slight re-orientation of all the dipoles towards its own direction, resulting in a magnetic moment proportional to the field. A field along the axis however has no effect on the ordering (corresponding to zero susceptibility in this direction) until its magnitude reaches a critical value at which it is able to produce re-orientation of the dipoles, the axes of alignment swinging away from the direction of the field, which then produces a magnetization comparable with that which the same field would give if applied perpendicular to the axis. The magnitude of this critical field depends on the anisotropy; its existence is a clear indication of antiferromagnetism. A very complete study of this kind has been made at Leiden by Gorter and his collaborators on $CuCl_2 \cdot 2H_2O$. This substance has its transition at 4.33°K.; at 1.6°K. the critical field is 6500 gauss. Besides magnetization and specific heat measurements, the Leiden work includes observations of "antiferromagnetic resonance" of the cupric ions and studies of the nuclear magnetic resonance spectrum of the protons in the waters of crystallization. These last give very detailed information on the antiferromagnetic state. The resonance frequency is proportional to the field, which is made up of the applied field together with the interaction field due to neighbouring magnetic particles. In $CuCl_2 \cdot 2H_2O$ the interaction field on a particular proton is chiefly due to the cupric ions, the next most important contribution being that due to the other proton of the same water molecule. Ignoring this latter, the proton resonance spectrum consists of four lines from the four different classes of protons, the frequencies at which these lines occur depending on the magnitude and direction of the applied field. Above the critical temperature the cupric ions undergo rapid changes of orientation, and their effective field is that due to their mean magnetization, and is thus parallel to and proportional to the applied field. As a result the proton resonance spectrum is displaced towards higher frequencies. Below the transition temperature however the rapid changes of orientation cease, and the ordering of the cupric ions results in a large interaction field independent of the magnitude of the applied field. Moreover, since the two sub-lattices are oppositely magnetized, the spectrum is practically symmetrical about the frequency corresponding to the applied field. The spectrum changes markedly when the applied field exceeds the critical value, since the magnetization of the sub-lattices is then perpendicular to the field, whereas at lower fields the axis of magnetization is independent of the field. A review of these experiments has been given by Poulis & Gorter (70). Further work on $CuCl_2 \cdot 2H_2O$ has been reported by Gerritsen, Okkes, Bolger & Gorter (71), by Van der Marel, Van den Broek, Wasscher & Gorder (72) and by Hardeman & Poulis (73).

Neutron diffraction and magnetic resonance studies give information on long range order in a crystal, whereas specific heats are affected by short

range ordering. It is therefore important to supplement purely magnetic studies by specific heat measurements. This point is well brought out by recent measurements on UI_3 by Roberts, Lavalle & Erickson (74) and by Roberts & Murray (75), and on $MnCl_2$ by Murray & Roberts (76, 77). The specific heat anomaly of $MnCl_2$ extends well above the transition temperature, in contrast with that of $MnCl_24H_2O$ [Friedberg & Waascher (78)].

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HETEROGENEOUS EQUILIBRIA AND PHASE DIAGRAMS[1]

By John W. Tierney and J. M. Smith
School of Chemical and Metallurgical Engineering, Purdue University, Lafayette, Indiana

INTRODUCTION

The task of the reviewer is complicated by the apparent contradiction in some of his objectives. In particular, the review should be understandable to the casual reader and yet inform the expert, and it should be comprehensive but not longer than twenty pages. Some compromises are necessary and the authors have decided that in this review the range of subject matter discussed would be limited to permit a more complete and critical analysis. It is felt that such a review will prove of more interest to the immediate user and also have a more lasting value than a superficial coverage of the entire subject of heterogeneous equilibria. The subject chosen for special attention is vapor-liquid equilibrium—with particular emphasis on equilibrium between organic liquids and their vapors. Attention will also be given to new and unusual developments in other areas.

For convenience this review has been divided into two parts—first, the experimental equipment and techniques used to obtain phase equilibrium data, and second, the correlation, interpretation, and prediction of phase equilibrium conditions. For those who are interested in particular systems, a tabulation of systems for which new experimental data were reported last year is given at the end of the review.

REVIEW OF EXPERIMENTAL METHODS

General.—The experimental determination of phase equilibrium data consists essentially of two parts—first, the intimate contacting of the phases at the desired conditions and for such a time that equilibrium is attained, and second, the measurement of the equilibrium phase compositions. It is preferable to measure the compositions while the phases are still in contact at the desired temperature and pressure. There is, then, no question of changes occurring between equilibration and measurement. More often, however, the temperature and pressure of measurement are determined by the analytical technique being used and are different than the equilibrium temperature and pressure. This introduces the possibility of changes in phase composition occurring between equilibration and analysis. If the system is one in which attainment of equilibrium is rapid, then ordinarily a sample of each phase must be obtained before the temperature and pressure can be changed. Systems of organic liquids and their vapors are of this type, and

[1] The survey of the literature pertaining to this review was concluded in January, 1956.

considerable care must be exercised to ensure that representative samples are obtained. Other systems, such as ceramic or metallurgical systems, reach equilibrium slowly, and the phases are usually left in contact during preparation for analysis—there being little danger that any significant change will occur before analysis. The analysis problem is much simpler when separation of phases has preceded sampling. A total chemical analysis is usually sufficient. If the sample is a mixture of phases, then complex analytical tools will be required to determine the properties of each phase. The experimental emphasis, therefore, is on sampling in systems which equilibrate rapidly and on analytic techniques in slower reacting systems. This emphasis will be apparent in the first section below, where the equipment and experimental techniques used to obtain vapor-liquid equilibrium data are discussed. In the second section, recent developments in experimental techniques for other systems are briefly reviewed.

Vapor-Liquid Systems

Methods of measuring vapor-liquid equilibrium can be classed in three groups—static methods, recirculation methods, and flow methods.

Static methods.—The material to be tested is put in a container, heated to the desired temperature, agitated until the phases have reached equilibrium, and then sampled. This method is mechanically simple and especially suited for extremes in temperature and pressure. The sampling step is the most troublesome because if material is withdrawn from the container the pressure will be changed unless the volume is changed also. However, as indicated previously, if the phases are analyzed in place, this problem is eliminated. Relatively little consideration seems to have been given this sort of measurement—probably because of the dependence on chemical methods of analysis in the past. The recent advances in measurement techniques should make the nonchemical methods of greater importance in the future. Mai & Babb (1), for example, measured vapor-liquid equilibria in the system CO_2—H_2S—Na_2CO_3—$NaHCO_3$—Na_2S—H_2O by a static method in which the liquid was analyzed by simultaneous measurement of pH and conductance, while the vapor was analyzed by using H_2S tagged with sulfur 35.

As indicated above, a constant volume container is difficult to sample. It is also difficult to obtain the desired pressure in the system during equilibration, and consequently, a container of variable volume is often used. The volume is controlled by adding or removing a fluid such as mercury. Obviously the system has then been increased by one component and one phase. If, as is always assumed, the new component is only present in the new phase, and, equally important, none of the other components are soluble in the new phase, then the system is unchanged. MacCormack (4) describes a static method in which the vapor space is separated from the liquid space by a stopcock. By closing the stopcock after equilibrium is attained, the vapor can be removed and analyzed. Considerable care must

be taken in the agitation procedure, however, to prevent any liquid from remaining in the vapor sample.

During the past year Todd (2) used a static method to investigate binary systems of ethylene with various polar and non-polar organic liquids of high molecular weight at pressures up to 1500 lbs./sq. in. Hogan (3) used a similar apparatus to investigate the ethane-ethylene system at −35°F. to 40°F. and up to 400 lbs./sq. in.

An indirect method of obtaining vapor-liquid equilibrium data is to measure the vapor pressure of a liquid mixture over a range of compositions and temperatures. A series of equations for the activity coefficients in the liquid as a function of composition can then be assumed and by comparing the calculated and observed pressures it is possible to determine when a suitable equation has been selected. Holtzlander (5) describes a suitable apparatus and presents some typical calculations. Since the method is indirect and the calculations laboricus, this method would only be of value when the vapor phase is difficult to analyze or sample.

Another similar technique is to observe the P-V behavior at constant temperature. The bubble and dew point pressures (saturated liquid and saturated vapor) can often be determined rather easily by direct observation. If the system is binary this is sufficient to give the vapor-liquid equilibrium curves because at a given temperature and pressure there can be only one liquid composition and one vapor composition in equilibrium. Dew and bubble points are also of interest in multicomponent systems, particularly naturally occurring hydrocarbons. It is sometimes difficult to visually detect the bubble or dew point, and other methods such as change in slope of P-V curve at constant temperature are used. Fokeev (6) describes a new technique using the reduction of the electrical capacity of a special condenser caused by gas bubbles appearing on the casing or lining of the condenser. He was also able to observe the kinetics of the gas formation.

Recirculation methods.—It is difficult to obtain large vapor samples when using static methods. Because of the large density differences, the volume of the vapor phase should be many times that of the liquid if approximately equal weights of each are to be analyzed. It then becomes difficult to ensure good contacting of liquid and vapor. One method of providing good contact is to remove the vapor and then bubble it through the liquid. Any size vapor sample can be provided by putting an appropriate amount of holdup in the vapor lines. An alternate method, and a much more generally used recirculation device, provides the equivalent of a very large vapor volume by continuously generating vapor, condensing it, and then returning the condensate to the boiler. By providing some liquid holdup in the condensate return line an adequate vapor sample is assured. The vapor sample is thus actually removed as a liquid (at a lower temperature, of course). This apparatus must be run long enough to ensure the attainment of steady state conditions. The condensate may be returned to the boiler as a vapor or as a liquid, the former being a vapor recirculation still and the latter a liquid

recirculation still. The difference is apparently trivial but is actually of considerable significance. If a vapor is returned (obtained by re-evaporating the vapor condensate) then additional transfer of mass between the liquid and vapor will continue until the steady-state equilibrium condition is reached. Liquid return, on the other hand, mixes with the liquid already present and is re-evaporated. The assumption must be made that the vapor generated from the liquid is in equilibrium with the liquid, an unproved assumption.

It should be pointed out here that no recirculation method in which the temperature of the vapor varies in passing through the apparatus is completely satisfactory if chemical reaction occurs in the vapor. Hall & Piret (7), for example, found that in the formaldehyde-water system there is a methylene glycol (formaldehyde monohydrate)—monomeric formaldehyde —water chemical equilibrium in the vapor phase which must be considered in addition to the vapor liquid equilibrium and that erroneous conclusions concerning the distillation of formaldehyde-water mixtures can be obtained if this equilibrium is neglected. Most recirculation stills condense the vapor with consequent alteration of the chemical equilibrium and are likely to be unsatisfactory if the rate of approach to chemical equilibrium is slow. Green & Vener (8) have reported data on the methanol-water-formaldehyde system using a liquid recirculation still. They state this is more satisfactory than a vapor recirculation still. It would seem that either a static system or a vapor recirculation system in which the vapor is not condensed would be better.

Liquid recirculation stills are the easiest to construct and operate and have been widely used. Othmer (9) in 1928 described an apparatus which is used today with only minor modifications (10). A constant volume holdup chamber is introduced into the vapor condensate line, and the overflow from this chamber enters the boiler. Othmer (11) recently proposed a modification in which the volume of holdup is variable and controlled by a stopcock. It is designed especially for determining the equilibrium flash vaporization curves for heavy petroleum fractions.

During the last year Rose & Williams (12) and Katz & Newman (13), described modifications of the liquid recirculation still in which the vapor generated in the liquid leaves through a tube so placed that slugs of liquid are entrained. The vapor and liquid are thus in intimate contact for some distance and equilibrium should be more easily attained. The liquid-vapor mixture from the tube impinges on a temperature measuring device and very accurate equilibrium temperatures can be obtained. The liquid and vapor are then disengaged and returned to the boiler. Provision is made for sampling of each stream after separation.

The vapor recirculation still proposed by Scatchard, Raymond & Gillman (14) has been widely used. In this design the vapors evolved from a boiler are bubbled through a liquid, then condensed and returned to the boiler. The liquid through which the vapors are bubbled is the equilibrium

liquid and, if the vapor is also in equilibrium with the boiler liquid, should be the same composition as the boiler liquid. A comparison of these two liquid compositions could be used to examine the assumption made in the liquid recirculation still that the vapor generated from a liquid is in equilibrium with the liquid. The operation of this still is made difficult by the fact that the liquid vapor contactor must be adiabatic and isothermal. If the vapors are superheated at all, there will be a loss of liquid. If there is any heat loss from the contactor, vapor will condense and there will be an accumulation of liquid. Hipkin & Myers (15) propose a design which maintains the contactor adiabatic by jacketing the reboiler and contactor.

Jones, Schoenborn & Colburn (16) obtained vapor recirculation by revaporizing the condensed vapor in a flash boiler. This system has only two liquid levels as compared to three in the Scatchard design and is easier to control. Amer *et al.* (17) describe a recent modification of the Colburn design.

Most recirculation stills use an inert gas to maintain the desired pressure in the condenser. Since there is a continual flow of vapor into the condenser there is no danger of inert accumulating in the vapor. However, there is always the possibility that the gas will be soluble in the condensate and be carried into the boiler where it might cause error. This danger is increased at high pressures.

Flow methods.—If equilibrium data are desired for an organic liquid near its decomposition temperature, recirculation methods or static methods cannot be used. The time required for equilibration may be sufficient to cause significant changes in composition. A flow method in which fresh material is continually fed to a heated tube is often used. Vaporization takes place in the tube at the desired temperature and pressure, and intimate contacting of the phases occurs. The phases are then separated and analyzed. The principle of operation is very similar to the liquid recirculation still which uses a Cottrell tube except that the equilibrium liquid and vapor are not returned to the boiler. Since the size of the vapor and liquid samples is determined only by the time the apparatus is run, it is often convenient to use a flow method where large samples are required. Intimate mixing in the tube is desirable from the equilibrium standpoint, but must not result in excessive pressure drop. This is especially significant in low pressure work.

Smith (18) describes a flow apparatus designed to measure the equilibrium between heavy petroleum residues and their vapors. It operates from about 1 mm. to 760 mm. Hg pressure and 400° to 800°F. The feed rate is about 0.5 gallons per hour. Vilim (19) describes an all glass flow still.

Other Systems

In this section experimental techniques used for equilibrium measurements in systems other than vapor-liquid are briefly reviewed. Because of space limitations only work published or abstracted during 1955 is included.

Further, only those articles that emphasize the experimental aspects of the problem or which seemed to contain a different technique are reported. In all cases the descriptions are brief and intended to indicate that a certain type of work was done rather than describe it in detail.

Differential thermal analysis (DTA) is a relatively new experimental technique that has found useful application in the study of clays and minerals. The sample being studied is heated slowly in a furnace under the same conditions as a sample of inert material. As phase changes in the sample take place, the temperature rises or falls below that of the inert. The temperature difference is recorded and is a very sensitive measure of the phase changes occurring. Lehmann & Fischer (20) discuss how these curves can be used to give quantitative evaluation of minerals. Similarly Wieden (21) used DTA curves to predict the compositions of mixed carbonates and impure carbonates. Accuracy was within 2 per cent up to 50 per cent dolomite. Eyraud & Goton (22) discuss the experimental requirements for high precision differential heat measurements and also suggest the possibility of using such data for kinetic studies. Wilburn (23) describes a completely automatic apparatus for DTA measurements, and Hiller & Probsthain (24) devised a method of protecting the apparatus from corrosive fumes when studying ores such as magnetic pyrites. Ivanov (25) used Kurnakov's pyrometer for DTA and calorimetric studies of microsamples, and Ravich *et al.* (26) used the pyrometer to study low temperature phase changes in microsamples. Murray & White (27) discuss the interpretation of DTA curves. They point out that since the isothermal decomposition of clay is a first order reaction, the clay is only 70 per cent decomposed at the peak temperature difference and that the heating rate has a marked effect on the curve obtained. Pelhan (28) also studied clay compositions. Mangold (29) claims that DTA is an inexpensive method of accurately correlating geologic formations from well to well. Some other interesting applications of DTA are to study building materials (30), to rank coals (31), and to study solid paraffin waxes (32).

In metallic systems, Nomarski & Weill (33) discuss the application of the method of interference of two polarized waves to metallography. This method is useful for the detection of small level variations on optically plane surfaces. The method is applied to the investigation of spiral growth of SiC single crystals, slip bands, grain boundaries, and twinning.

Rautala & Hyvärinen (34) discuss the instrumental error in x-ray diffractometers. They (35) also describe a method for separating the interference function and the structure function from x-ray diffraction pictures. The effects on the x-ray picture caused by crystal imperfections can thus be isolated and studied. In a third article (36) they use this method to determine crystal sizes in single crystals and grain size determination in fine powders.

Kogan & Pines (38) describe a method for determining the thickness and local composition of alloys of variable composition by measuring the ab-

sorption of monochromatic x-ray radiation. The same authors (39) also report a micromethod of phase analysis of alloys. High temperature Debye x-ray and electrical resistance measurements are used to study an alloy in a wire 0.05 mm. in diameter. Breitfeld (40) discusses the nondestructive testing of alloys by magnetic induction. Electrical conductivity is a measure of composition and can be measured by magnetic induction techniques. Apaev (41) studied the phase composition of annealed samples by determining curves for the intensity of demagnetization with temperature for steels annealed at 200°C.–600°C. Butters & Myers (42) used x-ray and neutron diffraction to study ternary alloys of Mn—Zn—C. Reshetkina (43) describes the use of surface oxidation methods for phase analysis of steels. Use of color photography is described. Lihl & co-workers (44, 45, 46) discuss the use of mercury amalgams to obtain low temperature phase equilibrium data in metallic systems. For example, in the system Cr—Zn, a Zn amalgam was prepared and then Cr electrodeposited on the amalgam (Cr is not very soluble in mercury). The mercury was then distilled off leaving a Zn—Cr powder which could be analyzed. Savings in labor and time are claimed.

Petrov & Bukhanova (47) describe an interesting method of obtaining equilibrium data. It involves the application of the Czochralski method for drawing single crystals from a melt to the drawing of a solid solution from the melt with which it is in equilibrium. As the solid solution is withdrawn, the melt changes composition and the solid solution must change composition also. By analyzing the rod withdrawn and relating its composition to the corresponding temperature of the melt, a solidus line in the equilibrium diagram is obtained. Other applications are also discussed.

Mosley & Lucchesi (48) describe an automatic instrument for the determination of critical solution temperature. Barthel & Dode (49) used radiobromine (Br^{82}) to study the vapor pressure of the bromine-CCl_4 system.

ANALYTICAL DEVELOPMENTS

Vapor-Liquid Equilibria

General.—The needs of industry for the compositions of gas and liquid phases in equilibrium can be broadly subdivided into two categories. Operations at medium pressures in the petroleum industry have required vapor-liquid equilibrium data for chemically similar mixtures under conditions where the liquid phase approached ideal solution behavior while the gas deviated strongly from the ideal gas law. On the other hand, separations in the chemical industry have usually involved chemically different substances, resulting in non-ideal liquid solutions, but frequently they have been carried out at low pressures so that the gas phase followed ideal behavior. Because of this situation, work on the development of methods for predicting vapor-liquid equilibria has been concentrated in these two areas. In recent years, the interrelationships between the chemical and petroleum industries and the need for treating chemical reaction equilibria more ac-

curately have increased the need for solutions to the more general problem of non-ideal gas and liquid phases. So far, progress on this complex problem has been slow.

Hydrocarbon systems.—The early work on phase equilibrium constants (ratio of composition of a component in the vapor and liquid phases) was based upon ideal solution fugacities, and hence gave results independent of composition. Such equilibrium constant charts (K charts) as those of Lewis (50) and Brown (51) were of this type and gave K values as a function of temperature and pressure.

The Kellog charts developed by Benedict and co-workers (52) represented the first effective attempt to predict K values as a function of the composition of the system. The theoretical background of this development was the calculation of fugacities of the vapor and liquid phases from the Benedict, Rubin & Webb (53) equation of state. This equation is an extension of the Beattie-Bridgman equation, designed to give improved agreement with experimental PVT data over a wider range of densities. The Kellog charts used the molal average boiling point as a single parameter to represent the complete composition of a phase. Even with this simplification, a large number of graphs were needed and some trial and error work is required for their use. In the last few years, the major effort in predicting phase compositions for hydrocarbon systems has been directed toward simplifying the Kellog charts. De Priester, in three papers (54, 55, 56), has revised and adapted the Kellog data so that the number of figures needed for the twelve light hydrocarbons has been reduced from 144 to 12. The form of the charts proposed by De Priester are easy to use when pressure interpolations are necessary.

The latest development in hydrocarbon work is that of Edmister & Ruby (57). Using the original Kellog charts, these authors prepared correlations giving the activity coefficients for hydrocarbons in the vapor and liquid phase as a function of three parameters: reduced temperature, reduced pressure, and boiling point ratio. This latter quantity is chosen to represent approximately the composition of the phase. It is defined as the ratio of the boiling point at atmospheric pressure for the component of interest divided by the molal average point of all the components in the phase. In this way, the number of charts required were reduced to six. Equilibrium constants can be computed readily from the activity coefficients in the vapor and liquid phases.

Through the past two decades many direct measurements, notably those of Sage *et al.* (58) have provided experimental measurements of compositions of the phases in equilibrium. These data and other experimental results have been of great value in utilizing theoretical methods based upon computed fugacities from an equation of state.

Nonhydrocarbon systems.—The methods of predicting vapor-liquid equilibria for non-ideal liquid systems have developed from application of the Gibbs-Duhem equation. Specifically, van Laar and Margules' solutions

have been used widely to correlate data for binary and ternary systems. Carlson & Colburn (59), in a pioneer paper, attempted to relate the most suitable type of solution to the chemical structure of the components of the system. A second significant contribution was the generalizations of Redlich, Kister & Turnquist (60), regarding the various types of solutions possible for the Gibbs-Duhem equation. These authors also proposed a useful form of using the equation for testing the accuracy and consistency of experimental vapor-liquid data. For a binary system, the test equation may be written

$$\int_0^1 \log (\gamma_1/\gamma_2) dX_1 = 0 \qquad 1$$

where γ_1 and γ_2 are the activity coefficients of components 1 and 2, and X is the mole fraction in the liquid phase. From a graphical viewpoint Eq. (1) requires that the net area under a plot of $\log (\gamma_1/\gamma_2)$ vs X_1 should be zero.

Broughton & Brearly (61) extended the idea of testing experimental data for consistency with the Gibbs-Duhem equation to the problem of refining data that are inconsistent. Their approach was to enumerate the systematic errors likely to influence vapor-liquid equilibria measurements and then develop a mathematical explanation for the magnitude of these errors. The test used to evaluate the data was similar to that proposed earlier (Eq. 1), but included the temperature term according to the equation

$$\int_0^1 T \log (\gamma_1/\gamma_2) dX_1 = 0 \qquad 2.$$

Inclusion of T improves the accuracy of using the Gibbs-Duhem equation for isobaric data where some temperature variation occurs.

Thyssen (62) has rederived the test equation of Redlich, Kister, & Turnquist (60) to account exactly for the effect of temperature variations. The resultant expression, analogous to Eq. 1, is

$$\int_0^1 -\left(\frac{\Delta L}{RT^2}\frac{dT}{dX_1}\right) dX_1 + \int_0^1 \log \frac{\gamma_1}{\gamma_2} dX_1 = 0 \qquad 3.$$

The importance of the temperature effect depends upon the liquid composition. For a 50 mole per cent mixture, the error introduced by using the simpler Eq. 1 is negligible, while at either end of the composition range it may be large.

The van Laar and Margules solutions can be shown to represent the first few terms of infinite series expressions for the excess free energy of mixing. The application of these methods to ternary systems requires, as a minimum, experimental data for each of the possible binary systems. Likewise, quaternary systems would require experimental data for each of the constituent ternary mixtures. For this reason, the van Laar and Margules equations are not convenient for multicomponent systems. However, the Margules equation with four terms has been used to correlate the data of the ternary system of styrene-ethylbenzene-acetic acid (63). Recent applications

of the van Laar equation include the systems methylcyclohexane-toluene (64) and octane-ethylbenzene (65).

Using the Yu-Coull method (66), Garner & Hall (67) studied the methyl cyclohexane-toluene-furfural system. Experimental data were obtained on each of the three constituent binaries as well as the ternary, and the results satisfactorily correlated by the Yu-Coull scheme. One of the most promising of the procedures for predicting ternary results from binary data is that of Pigford *et al.* (68). Studies of the acetone-methanol-chloroform, acetone-methanol-carbon tetrachloride, and acetone-methanol-methyl acetate systems indicated that three and four suffix Margules equations represented the binary and ternary data. For mixtures in which all deviations from Raoult's Law are positive, it was found that no ternary data were needed to evaluate the constants in these equations. When deviations from Raoult's Law were not all positive, a single ternary constant was required.

Applying a different approach to the problem, Hirata (69) has presented a method of predicting ternary, vapor-liquid equilibrium data from boiling point information on the ternary system. Such data are easier to obtain experimentally than the equilibrium phase compositions themselves.

Equilibria Involving Solid Phases or Metals

Lebedev (70) has attempted to classify the phase diagrams of binary alloys in accordance with the degree of reaction between the components. The diagrams range from horizontal lines, corresponding to no reaction, to the complex case of complete reaction in the liquid and solid phases resulting in the formation of one or more compounds. This work should serve as a useful method of classifying binary alloys and for breaking down a complex system into simple, component parts.

The applications of the Gibbs-Duhem equation to ternary systems is of considerable interest in metallurgical work, and solutions of the equation have been proposed by Darkin (87) and Wagner (88). Recently (89), a new method has been developed, which is based upon the use of isoactivity curves on the triangular phase composition diagram. The basic equation in the procedure is readily derivable from the Gibbs-Duhem relation and may be written,

$$\left(\frac{\partial \mu_2}{\partial \mu_1}\right)_{n_2,n_3} = -\left(\frac{\partial n_1}{\partial n_2}\right)_{\mu_1,n_3} \qquad 4.$$

where μ represents the chemical potential, n the number of moles, and the subscripts refer to components 1, 2, and 3 of the system. The right hand derivative represents the tangent to the isoactivity curves for component 1 on the triangular diagram. In the development, this concept of isoactivity tangents leads to a graphical method of constructing constant activity lines. Equation 4 illustrates that the chemical potential (or activity) of two components may be evaluated from isoactivity curves for the third component of the ternary system.

Schuhmann has illustrated his method by constructing constant activity curves for SiO_2 and FeO from experimental data for the activity of oxygen in iron-silicate slags.

The types of equilibria involved in geologic processes are reviewed by Ramberg (71). The chemical equilibria processes involve reactions between solid phases. In nature these processes are too complex to be described exactly by thermodynamic methods. However, the author indicates interesting and possibly useful approximate forms of analyses for such systems.

The phase behavior of ceramic materials was adequately reviewed in 1953 by White (72). This paper gives an excellent presentation of the application of the phase rule and the concept of minimum free energy to such processes as phase changes, dissociation of oxides, formation of solutions, and fusion relations in binary systems. The thermodynamic properties of ionic phases are discussed in some detail.

The accurate calculation of simple binary and ternary phase diagrams for refractory systems has been accomplished (73) by activity calculations in the molten salt-fluoride solvent solutions. The activities are evaluated from entropy estimates based upon structural information and statistical thermodynamics. The results were good for the systems: MnO—Al_2O_3, MgO—BeO, Al_2O_3—ThO_2, Al_2O_3—ZrO_2, CaF_2—NaF, and LiF—KF—NaF. Calculated diagrams for systems containing UO_2 did not agree with the experimental data. It is suggested that the reason is an erroneous value for the heat of formation of UO_2. If 1700 cal./g. mole were used instead of the accepted 2400 value, the computed curves would agree with experimental solid-liquid phase boundaries.

Using a theory originating with Smirnov (74), Krivoglaz (75) has computed the solubility of a third element in the interstices of the crystal lattice of a binary alloy. The agreement obtained in the two examples considered, hydrogen in palladium-platinum and in iron-vanadium alloys, was good. In the latter case, the experimental solubility of 24 per cent at 1200°K. was predicted exactly. The theory is based upon a vacancy concept in which only nearest-neighbor interactions are considered. The equilibrium concentration of vacancies was expressed as a function of the concentration of the solid solution. Then the potential barrier to the transfer of an atom to a neighboring vacancy was also found as a function of concentration. Finally, the diffusion coefficient was computed and then the solubility.

The available information on activities in equilibrium solutions of metallic systems was enriched during the year with several papers on systems including iron (76, 77, 78). Experimental measurement of dissolved oxygen content was used to determine the activity of PbO in SiO_2 at temperatures from 1000–1194°C. by Richardson & Webb (79). Semi-quantitative activities of FeO, SiO_2 and CaO were evaluated by Elliott (80) in the ternary system at 1600°F.

The equilibrium constant for the reaction

$$2B + 3H_2O = B_2O_3 + H_2$$

was evaluated by Yagihashi (81). Boron was dissolved in liquid iron and water and hydrogen constituted the gas phase in equilibrium with the liquid. Using tin solution calorimetry, Rubin (82) studied the energy of formation of ordered and disordered solid solutions of Cu_3Au. Sanbongi (83) measured the equilibrium concentration of silicon in iron in the iron-slag system. The equilibrium constant for the following reaction was obtained:

$$SiO_2 \text{ (in } CaO—Al_2O_3 \text{ slag)} + 2H_2 = Si \text{ (in iron)} + 2H_2O$$

The nature of the ternary deoxidation diagram of O, C, and Al was studied by Yagihashi (84) by carrying out the deoxidation of alumina in a carbon crucible using pure carbon monoxide at temperatures from 1650 to 2050°C.

Equilibrium constants for the formation of metal hydrides and for nitrogen in iron and steel are considered by Pearson & Ende (85). The pressure-temperature relationships involved in the vacuum separation of ternary systems are presented by Müller (86). The specific requirements are considered for the separation process applicable to Ag—Zn—Pb systems.

Experimental Data

Many articles during the past year reported new experimental phase equilibria data. For the benefit of those who are interested primarily in certain systems, a tabulation of much of this work is given below. Data have been divided into five groups—metallic systems, oxide systems, organic systems, aqueous salt systems, and anhydrous salt systems. In each subdivision, a particular system has arbitrarily been listed under that element or compound whose chemical symbol is first alphabetically.

Metallic Systems

Ag —Ce—La (187); —Cr (90); —Co—Pd (91); —Co (111).

Al —As (93); —Si (94); —Ti (95); —Cu—Ni (96); —Mg—Li (97); —Cu—Mg—Si (98)

As —Ga (93)

Au —Pt—Pd (37); —U (208)

Be —C—U (209)

C —V (210); —Mn—Fe (92); —Ni—Fe (99)

Cd —Ge—Sn—Zn—In (100); —Ce (101); —La (101); —Pr (101)

Ce —La (102); —In (102)

Co —In (103); —Cr—Mo (104); —V (105)

Cr —Pt (106); —Rh (106); —Ru (106); —Pd (107); —Ni (108); —Fe—V (109); —Ni—Ti (110); —Fe—O (131)

Cu —Pd (111)

Fe —Ti (112); —P—V (113); —P—W (114); —U—Ni (115); —Mg—Cr—Al—O (146)

Ga 12 binary diagrams, 70 ternary diagrams, and 19 quaternary diagrams) (116); —Sb (117); —Sb (93)

Ge —Re (118); —Ti (119)

In 26 binary diagrams and 6 ternary diagrams (120); —Pb—Sn (121)

Ir —Mn (122)

Mg —Ti (123)

Mn —Pt (122); —Rh (122);

—Ru (122);
—Ta—O (132);
—U—Ni (115)

Ni —Sb (124); —Ti (125); —Re (126); —Zr (126)

Pb —Ti (127)

Pd —Si (128)

Sn —Ti (95)

Th —U—Zr (129)

V —Zr (130)

Oxide Systems

Al_2O_3 —B_2O_3—SiO_2 (133); —MgO—SiO_2—ZrO_2 (147)

B_2O_3 —P_2O_5—SiO_2 (134)

BaO —TiO_2 (135)

BeO —TiO_2—ZrO_2 (136); —CeO_2—ZrO_2 (136); —Cr_2O_3—ZrO_2 (136); —In_2O_3 (137)

CaO —TiO_2—SiO_2 (138); —Fe—Fe_2O_3 (139); —TiO_2 (140); —SiO_2—H_2O (141); —ZrO_2—TiO_2 (142); —FeO—SiO_2 (143)

CeO_2 —Ce_2O_3 (144)

Cr_2O_3 —MgO—SiO_2 (145)

FeO —Fe_2O_3—SiO_2 (148)

La_2O_3 —ZrO_2 (149)

Li_2O —MgO—SiO_2 (150)

MgO —ZrO_2—TiO_2 (142); —CaF_2—SiO_2 (151)

Na_2O —FeS—SiO_2 (152)

Nd_2O_3 —ZrO_2 (149)

PrO_2 —Pr_2O_3 (144)

SiO_2 —TiO_2 (153)

Aqueous Salt Systems

Al_2O_3 —P_2O_5—H_2O (154)

B_2O_3 —Li_2O—H_2O (155), (161)

$BeSO_4$ —$MnSO_4$—H_2O (156); —$FeSO_4$—H_2O (157)

Cr_2O_3 —P_2O_5—H_2O (158); —H_2O (159)

HgS —Na_2S—H_2O (160)

LiCl —MCl_2—H_2O (162) where M = Be, Ca, Sr, Ba, Zn, & Cu

MgO —$MgCl_2$—H_2O (163)

$Mg(BrO_3)_2$ —H_2O (164)

NaOH —NaCN—H_2O (165); —H_2O (166)

Na_2O —P_2O_5—H_2O (167); —UO_3—H_2O (168)

NaCl —Na_2SO_4—$CaSO_4$—H_2O (169); $NaOCl_2H_2O$ (170)

N_2O_5 —H_2O (171)

P_2O_5 —H_2O (172)

Sc_2O_3 —H_2O (159)

Tl_2O_3 —H_2O (159)

Organic Systems

H_2 —C_2H_4 (173)
C_3H_6 (173)
C_3H_6 (173)
C_3H_8 (173)

CH_4 —C_2H_6 (174)
—C_3H_8 (175)

C_3H_8 —CO_2 (176)

nC_4H_{10} —N_2 (177)

nC_6H_{14} —C_6H_{12}—NH_3 (178)

nC_7H_{16} —C_8H_{16}—NH_3 (178)
—N_2 (179)

$C_6H_5NH_2$ —C_6H_6 (180)
—C_6H_{12} (180)

C_2H_5OH —C_6H_6 (181)

nC_4H_9OH —CH_3OH (182)
—$(C_2H_5)_2O$ (182)
—*iso* C_4H_9OH (182)

CCl_4 —CH_3CN (183)

CH_3NO_2 —C_6H_6—C_6H_{12} (184)

H_2O —l—C_4H_8 (185)
C_6H_6—CH_3COOH (186)
—HCHO—CH_3OH (8)
—CH_3OH (8)
—HCHO (8)
—$CH_3CH_2CH_2$ COOH (188)
—HCOOH (189)
—pyridine (190)

H_2O —CH_3COOH—$CH_3CH_2CH_2$-CH_2OH (191)
—diacetone alcohol (192)
CH_3COOH
—CH_3COOCH_3 (193)

Anhydrous Salt Systems

$AlBr_3$ —$(C_2H_5)_2O$—$C_2H_4Br_2$ (194); $SbBr_3$—$C_2H_4Br_2$ (194)
$Ba(NO_3)_2$ —KNO_3 (195)
BeF_2 —LiF (196); —PbF_2 (196)
CaI_2 —CaF_2 (197)
$CeSO_4$ —$MgSO_4$ (198)
KPO_3 —$NaPO_3$ (199); $K_4P_2O_7$ (199)
$MgSO_4$ —Rb_2SO_4 (200)
Na —NaF (201); —NaCl (201); —NaBr (201); —NaI (201)
UF_6 —Br_2 (202); —BrF_3 (203); —BrF_5 (203)
Na, K‖Cl, SO_4 (204); Li, K‖SO_4, WO_4 (205)
K, Co‖Cl, SO_4 (206); Na, PbO‖F, TiO_3 (207); Na, Pb‖TiO_3, $MoO_4(WO_4)$ (207)

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SOLUTIONS OF NONELECTROLYTES[1]

By Robert L. Scott

Department of Chemistry, University of California, Los Angeles, California

1955 was a year of steady progress in the field of nonelectrolyte solutions. No striking new theories were offered, although some older ones were analyzed, criticized, and sometimes modified and extended. A large amount of good experimental work was reported, some of major importance. Some of these observations could be interpreted within the framework of existing ideas, some required new interpretations, and some are as yet without explanation. All in all, it was a fairly typical year.

The writer has attempted to include all the 1955 papers which he found of interest and importance. Mere experimental measurements, devoid of apparent wider interest, have not been discussed, and some important papers have almost inevitably been overlooked; for this, apologies are offered to their authors and to the reader.

The author of this review has at times not hesitated to express an opinion upon some subjects which are certainly still controversial. He believes, as have most of his predecessors in this series, that a good review cannot avoid this; a mere list or compendium of facts is almost useless.

Mixtures of Gases

Since slightly imperfect gases offer the simplest examples of the influence of intermolecular interactions upon thermodynamic quantities, they have been exhaustively studied in attempts to get accurate data on the second virial coefficient and its temperature dependence, and from this, information about the potential energy function of a pair of molecules. Similarly, from measurements on gas mixtures, one can deduce a second virial coefficient B which can be shown to be made up of three terms.

$$B = x_1^2 B_{11} + 2x_1 x_2 B_{12} + x_2^2 B_{22} \qquad 1.$$

The coefficients B_{11} and B_{22} are those for the pure components and depend upon the potential energy functions of a pair of identical molecules, but B_{12} arises from the interactions of an unlike pair. The simplest potential functions involve only two parameters, the energy ϵ_{ij} of a molecular pair at its equilibrium distance and the (low temperature) collision diameter σ_{ij}, and may be written in the general form:

$$u_{ij}(r) = \epsilon_{ij} f(\sigma_{ij}/r) \qquad 2.$$

where f is a universal function of the reduced variable σ/r. Careful measurements of B_{12} yield information about u_{12} and dictate a choice of appropriate combination rules for calculation of the 1,2 parameters from those for the

[1] The survey of the literature pertaining to this review was completed in January, 1956.

pure substances, information which can be carried over to theories of liquid solutions.

Mason (1) has used an intermolecular potential function with an exponential repulsion term to fit data on a series of binary gas mixtures of H_2, He, Ne, A, Kr, Xe, and CH_4. With the set of three parameters for each pure substance and a reasonable set of combining rules (either arithmetic means or geometric means) he calculates values for the second virial coefficient of the mixture and several non-thermodynamic properties (viscosity, thermal conductivity, diffusion, thermal diffusion) which are sometimes in excellent agreement with experiment, and are always reasonable. The author notes that a simpler potential, the Lennard-Jones six-twelve with a geometric mean for ϵ_{12} and an arithmetic mean for σ_{12}, would have yielded nearly as good agreement throughout. Kihara & Koba (2) have used the former's "core" model of nonspherical intermolecular forces to fit B_{12} data on a number of binary systems.

Francis & McGlashan (3) have measured second virial coefficients for carbon tetrachloride and chloroform and for the mixtures carbon tetrachloride-chloroform and chloroform-benzene. The results fit a law of corresponding states well (e.g. a two parameter potential function) but the components are too similar for one to choose between the Lewis and Randall rule ($2B_{12} = B_{11} + B_{22}$) and the Guggenheim and McGlashan combination rules (arithmetic mean for cube root of critical volume; geometric mean for critical temperature).

Waelbroeck (4) has determined second virial coefficients for benzene-cyclohexane mixtures, and used the constants derived therefrom for interpretation of the liquid mixture.

Hamann, Lambert & Thomas (5) made careful measurements on mixtures of methane-neopentane, methane-tetramethylsilane and methane-sulfur hexafluoride, and found the second virial coefficients did not conform to the Guggenheim-McGlashan treatment, because of the inapplicability of the principle of corresponding states and because of the inaccuracy of the geometric mean law for T_c (i.e. for ϵ). The authors offer a plausible explanation in terms of non-central forces for all but the methane; a crude theoretical treatment predicts deviations in the direction observed, and of about the right magnitude. Deviations are greatest for the CH_4-SF_6 system.

General Theory

As always, the goal of theories of nonelectrolyte solutions is to calculate the properties of mixtures from the properties of the pure substances and a minimum number of parameters describing the interaction between unlike components. No 1955 publication brought us much closer to this goal, but several give us a clearer understanding of some of the difficulties.

Corresponding states theories.—Several recent treatments of solutions have been based fundamentally upon the principle of corresponding states [Longuet-Higgins (6); Prigogine & Mathot (7); Salsburg & Kirkwood (8);

Prigogine & Bellemans (9)]. All assume that the potential energy of interaction $u_{ij}(r)$ between two molecules i and j can be expressed in a universal reduced form like Eqn. 2. Then both pure liquids conform to the same reduced equation of state, a function of a reduced temperature kT/ϵ and a reduced volume V/σ^3, and in principle, all properties of a mixture of the two (expressed as functions of T, P, and x) are determined by specifying six parameters: ϵ_{11}, ϵ_{12}, ϵ_{22}, σ_{11}, σ_{12}, and σ_{22}.

Actually, if an appropriate reference state is selected, any property of the solution can be expanded around this reference point in a Taylor series involving four variables: $(\epsilon_{22}-\epsilon_{11})$, $(\sigma_{22}-\sigma_{11})$, $(2\epsilon_{12}-\epsilon_{11}-\epsilon_{22})$ and $(2\sigma_{12}-\sigma_{11}-\sigma_{22})$. If the arithmetic mean for the two pure components is chosen for the reference state, the coefficients of the first order terms in $(\epsilon_{22}-\epsilon_{11})$ and $(\sigma_{22}-\sigma_{11})$ vanish identically, and the coefficients of the other two have been shown unequivocally to be $2E_0/(\epsilon_{11}+\epsilon_{22})$ and $6(PV_0-RT)/(\sigma_{11}+\sigma_{22})$ respectively where E_0 and V_0 are the molar cohesive energy and molar volume of the reference state. The coefficients of the second order terms—squares and cross products—have been formulated by Brown & Longuet-Higgins (10) but cannot be directly related to any thermodynamic properties of the reference species. This difficulty becomes especially important if one makes the common assumptions that $\epsilon_{12}=(\epsilon_{11}\ \epsilon_{22})^{1/2}$ and $\sigma_{12}=(\sigma_{11}+\sigma_{22})/2$. Then $(2\sigma_{12}-\sigma_{11}-\sigma_{22})$ vanishes, while $(2\epsilon_{12}-\epsilon_{11}-\epsilon_{22})$ is proportional to $(\epsilon_{22}-\epsilon_{11})^2$; any calculations therefore depend crucially upon the uncertain second order terms. Longuet-Higgins' conformal solution theory is thus applicable only when $(2\epsilon_{12}-\epsilon_{11}-\epsilon_{22})$ is effectively first order; some of the examples he cited probably fit this criterion, but most solutions of nonpolar nonelectrolytes do not.

Waelbroeck (4) has shown, using his data on the gas mixtures, that the Longuet-Higgins $d_{12}[=(2\epsilon_{12}-\epsilon_{11}-\epsilon_{22})/\epsilon_{11}]$ is actually 0.00 ± 0.02 for benzene-cyclohexane, although a value of -0.065 is needed to fit the data to the first order conformal solution theory; he concludes therefore that the primary contributions here are from second and higher order terms.

Englert-Chwoles (11) has discussed various sources of the excess entropy, largely within the limits of the cell theory, and has cited evidence for a parallelism between the excess entropy and the volume change.

Rowlinson & Sutton (12) have considered the further complication that nonspherical molecules (e.g. all but the rare gases and methane) have more involved potential energy functions than Eqn. 2 and have extended the first order theory of Longuet-Higgins to include another set of variables. Cook & Rowlinson (13, 14), had found, as Pitzer & coworkers (15, 16) have since reemphasized, that the thermodynamic properties of non-polar and not too highly polar substances deviate from those predicted by a law of corresponding states in a way which can be satisfactorily interpreted by the introduction of a single additional variable (which they called δ, but which we here call h, to distinguish from the solubility parameter). The principal effect of their inclusion of $(2h_{12}-h_{11}-h_{22})$ is to admit another adjustable parameter

with which the authors can fit data on systems where the less flexible conformal solution theory fails (e.g. benzene-cyclohexane); "second-order" effects are ignored. That this effect exists no one can doubt, and the authors' application of their theory to vapor-liquid equilibrium in binary systems of CO_2, N_2O, C_2H_6, and C_2H_4 (17) is more convincing evidence of its importance.

The present status of "solubility parameter" theory.—For about a quarter-century much of the interpretation of the properties of nonelectrolyte solutions, particularly those involving only non-polar components, has developed around equations formulated by Hildebrand and by Scatchard. In its present form (18), the equation for the free energy of mixing may be written:

$$\Delta F^M = RT(x_1 \ln x_1 + x_2 \ln x_2) + (x_1V_1 + x_2V_2)(\delta_1 - \delta_2)^2\phi_1\phi_2 \qquad 3.$$

where V is molar volume; x, mole fraction; ϕ, volume fraction; and δ, the "solubility parameter," is the square root of the cohesive energy density, $-E/V$, for the pure component.

The various derivations of Eqn. 3 all involve some rather sweeping assumptions about the randomness of position and orientation of molecules in the solution. The first term in Eqn. 3 is the configurational part of the free energy and is frequently identified with the entropy of mixing; a solution with ideal entropy of mixing and non-zero heat of mixing is a "regular" solution. Probably no exactly regular solution exists (alas, "strictly regular" has an even more circumscribed meaning), but it is convenient as a limiting standard of behavior for solutions. For many solutions, the excess entropy of mixing is indeed small (particularly when corrected to constant volume conditions) compared with the heat of mixing.

Mauser & Kortüm (19) have challenged the use of the concepts of "regular" solutions and "athermal" or "semi-ideal" solutions on the grounds that it is impossible to pass continuously from the ideal gas mixture to the liquid mixture by any process in which one property of the gas mixture (zero excess entropy or zero heat of mixing) is maintained and not the other. It does not seem necessary, however, to define these solutions in a way which requires them to retain their properties over the entire range of temperatures and pressures (this would exclude "ideal" solutions, too); a nonzero range of T and P will suffice.

Moreover, various perturbations (order-disorder effects, volume changes, etc.) which modify the entropy of mixing tend to modify the heat of mixing as well, and in such way as to leave the free energy function relatively unchanged. The only major change in the configurational term of Eqn. 3 which has been suggested is the substitution of the Flory-Huggins term ($x_1 \ln \phi_1 + x_2 \ln \phi_2$) for ($x_1 \ln x_1 + x_2 \ln x_2$) in order to allow for differences in size between the two components. This formulation is not exactly right for the solutions of long chain polymers for which it was designed, and the wisdom of its application to solutions of ordinary molecules seems doubtful, at least to this writer; it is almost certainly an overcorrection for the size effect.

More important however is the reliability of the second term of Eqn. 3 as

a measure of the change in molecular interaction energy upon mixing. To write this as a product of the square of the difference in properties of the pure components we must make the usual geometric mean assumption about ϵ_{12} or something nearly equivalent. For a variety of reasons, one of which we shall discuss later, it is doubtful if this can ever be exactly true, and for polyatomic molecules of widely varying sizes and shapes, it is not easy even to estimate how far off this approximation is.

What may seem surprising is that Eqn. 3 has proved useful at all. Yet it, or its variant with the Flory-Huggins configurational term, has been useful in interpreting qualitatively and often semiquantitatively a wide variety of nonelectrolyte solutions including those of high polymers; especially so when the components are nonpolar and when solubility phenomena are involved. Other theories (e.g. one of the corresponding states variety) often prove more successful for a narrowly restricted group of systems which conform to a special model, but no other has nearly as wide a range of usefulness.

The reason for this success seems to rest upon two features:

First: The theory behind Eqn. 3 does not rest upon any special model, but rather upon two general, semi-intuitive assumptions, one about randomness, and the other about the 1-2 interaction. Probably neither can be exactly correct, but as formulated neither is likely to be terribly wrong, at least with nonpolar substances.

Second: Solubility is usually a rather gross phenomenon, frequently (always in the case of liquid-liquid immiscibility) involving large deviations from ideality in the solution phases; excess free energies far in excess of thermal energies are not uncommon ($\overline{F}_2^E$ for I_2 in C_7F_{16} is 4300 cal. at 25°C.). Here an unpretentious theory "built close to the ground" might well show a measure of success.

Solubility parameter theory does in fact fit the free energy data on most binary systems of nonpolar nonelectrolytes to within 10 to 20 per cent of thermal energies (60–120 calories per mole at 25°C.) or to within the experimental uncertainty of the solubility parameters (which is sometimes large); for heats and excess entropies of mixing, it is somewhat less successful. Considering its almost complete lack of a precise model, it could hardly be expected to give much better agreement; all kinds of minor perturbations can give rise to contributions of magnitudes of small fractions of RT. On the other hand, it follows that when solubility parameters appear to give correct predictions of small values of F^E, etc., the agreement is probably merely fortuitous.

In short, the solubility parameter equations offer a useful initial approach to a very wide area of solutions, like a small scale map for a very broad long distance air view of a subcontinent. It is able to make numerical predictions about all areas; these are unlikely to prove highly accurate when a small area is examined carefully, but they are equally unlikely to prove completely absurd. A really serious failure of solubility parameter theory

implies qualitative failure of the basic assumptions and attracts serious attention, as we shall see in a later section.

Other theories.—No corresponding states theory can offer much hope of being useful with solutions of two substances of radically differing molar volumes (i.e. when $\sigma_{22}-\sigma_{11}$ is large); for these the regular solution-solubility parameter treatment remains much superior. Alder (20) has calculated, with the aid of the superposition approximation, the thermodynamic properties of a binary mixture of nonattracting rigid spheres with a radius ratio of 3:1 at several mole fractions and at several densities; a mixture of spheres of various sizes permits more economical packing than when the spheres are of uniform size.

Buff & Brout (21) have extended the earlier molecular distribution function treatments of McMillan & Mayer (22) and Kirkwood & Buff (23) and have succeeded in obtaining expansions in powers of the volume fraction of solute (at constant temperature and pressure) for partial molar free energies. energies, and volumes. Specific molecular models will have to be used to get the necessary distribution functions, but the authors suggest that their rigorous expressions imply relationships among the thermodynamic variables and composition fluctuations which may have been violated by earlier model theories.

It is evident that we need to know much more about the properties of pure liquids and develop a more nearly adequate theory of liquids before much further progress can be expected in basic theories of solutions. This fact was emphasized by the measurement of the internal pressure of carbon tetrachloride by Benninga & Scott (24). They found that, over a 75 degree temperature range, the ratio of the internal pressure $(\partial E/\partial V)_T$ to the cohesive energy density $(-E/V)$ is virtually constant at a number very close to unity (1.08); this result is in good agreement with the predictions of the old van der Waals theory, but disagrees radically with the predictions of the Lennard-Jones and Devonshire cell model which has been widely used as a basis for theories of solutions (7, 8, 9).

Hildebrand (25) has reviewed the history of the osmotic pressure concept, and how it has influenced the development of theories of nonelectrolyte solutions.

Kikuchi (26) has developed another method for deriving the rigorous equation of state for a one-dimensional binary solution; for a lattice model, the equations reduce identically to those obtainable by the quasichemical approach.

Bueche & Krigbaum (27) have examined the effect of the choice of cell size upon the calculation of entropies of mixing by counting configurations in a lattice model. If one makes the usual Flory approximation that the probability f_i of finding a particular site vacant is equal to the fraction of sites already filled, the entropy of mixing is independent of the cell size, whether that is larger, smaller or equal to the molecular volume of the smaller component. The authors conclude that an effect of chain flexibility

can appear only in deviations of the probability f_i from the Flory value.

Kurata, Tamura & Watari (28) have carried the theory of combinatory factors (such as the Flory f_i) to higher approximations. They show that the Bethe approximation (or the equivalent Guggenheim treatment) assumes a "dendritic" lattice, in which there can be no closed rings of interactions, regardless of the number of elements in the ring; only in their further ("second") approximation, in which closed rings explicitly appear, does flexibility of chains play a role.

Kurata & Isida (29) have used the approximate Flory equations for the thermodynamics of polymer solutions in treatment of pure paraffin liquids; the straight chain hydrocarbon molecule occupies multiple sites in a lattice where the monomeric solvent consists of "holes" (vacant sites). Considering the simplicity and crudity of the model, the agreement with experimental data on critical constants, boiling points, and heats of vaporizations is remarkably good.

Huggins (30) has recast his derivation of the Flory-Huggins equation in a form which is at least formally applicable to all kinds of nonelectrolyte solutions; all deviations from the simple theory appear in the parameter μ, which may be concentration dependent.

No attempt can be made here to cover the extensive literature on high polymer solutions; the papers cited above seem to be relevant in the treatment of solutions of molecules of short chain length as well. For further information, the reader is referred to the chapter on Polymers.

Critical Phenomena

This year has seen a continuation of the search for a satisfying interpretation of the curious behavior of two component liquid-liquid mixtures near the critical solution temperature and the analogous behavior of one component liquid-vapor equilibria near the critical point. For sometime, it has been apparent that over a remarkably wide range of temperatures, the coexistence curve fits a relation of the form $T_c - T = k(x'' - x')^n$ where x'' and x' are the mole fractions of one component in the two conjugate phases, and n is approximately three, rather than two as predicted by classical van der Waals theory. Rice (31) has reviewed his measurements of the system cyclohexane-aniline with Rowden (32) and with Atack (33, 34) and has reaffirmed his belief that the coexistence curve has a flat top. He finds that below his flat top, the experimental data are in excellent agreement with an equation

$$T_c - T + \delta = k(x'' - x')^3 \qquad 4.$$

where δ is the temperature difference between the flat top and the maximum of the extrapolated cubic curve. For cyclohexane-aniline, $\delta = 0.005°C.$, while for perfluoromethylcyclohexane-carbon tetrachloride, the system earlier investigated by Zimm (35), Gopal & Rice (36) find $\delta = 0.001°C.$ In this latter case, δ is no greater than the limit of temperature fluctuation of the bath, and the authors admit that a rounded top is not excluded.

Krichevskii, Khazanova & Linshitz (37, 38) have made dilatometric studies of the systems phenol-water and triethylamine-water and report that the curve of specific volumes is parabolic.

Rice (39) has developed a thermodynamic theory of one component liquid-vapor critical phenomena which, while he does not do so, can presumably be extended to the analogous liquid solution case. His only major assumption is that $(\partial^2 P/\partial T \partial V)$ is finite, non-zero, and continuous throughout the one phase region; it then follows that the critical isotherm has the form $P - P_c = k(V - V_c)^{n+1}$ where n is the exponent in the coexistence curve. If n is greater than two, it follows that C_v (and *a fortiori* C_p) will have an infinite discontinuity at the critical point of a round-top coexistence curve, a conclusion in line with an earlier suggestion by Scott (40). If the top of the coexistence curve is flat, as Rice believes, the infinity (but not the discontinuity) is avoided. Krichevskii & Kazanova (41) have offered another thermodynamic treatment of critical phenomena.

Skripov & Semenchenko (42) have measured C_p for a series of triethylamine-water mixtures and find, as have other workers before them (43) the expected large discontinuities at the phase boundary; they have also investigated (44) the effect of added $(CH_3)_4NI$ upon the heat capacity in the critical region.

Kohler (45) has developed a formal theory which assumes a symmetrical equation for the excess free energy of a system

$$F^E(T, x) = wx(1 - x)\psi(x) \qquad 5.$$

Here w is a constant, the usual interchange energy, and $\psi(x)$ is a function, apparently independent of temperature, which purports to measure the deviation of the number of unlike nearest neighbors from that in an ideal (randomly arranged) solution. In order to fit the experimental coexistence curves, $\psi(x)$ must be a function with a double maximum.

Liquid Mixtures: Thermodynamic Properties

Staveley, Tupman & Hart (46) have reported careful measurements of the heat capacity, the coefficient of thermal expansion and the adiabatic compressibility over a range of temperatures from 20° to 70°C. for four binary mixtures: benzene-carbon tetrachloride, benzene-1,2-dichloroethane, acetone-chloroform, and acetone-carbon disulfide. With these data, and existing data on ΔF, ΔH, and ΔV, they calculate C_v (already discussed in a previous paper (47)), the energy and excess entropy of mixing at constant volume and related quantities. $TV^2(\partial P/\partial T)_v$ (the van der Waals a) is remarkably constant over a wide temperature range; for all four systems, this quantity fits closely the Hildebrand-Carter equation: $a = (x_1 a_1^{1/2} + x_2 a_2^{1/2})^2$. This is equivalent to assuming a geometric mean relation for a parameter a_{12}, and its success might be cited as support for use of the geometric mean for the related quantity ϵ_{12}; at least for the acetone-chloroform system, with its negative heat of mixing, this would be far from correct.

Copp (48) has measured the total vapor pressures of water-methyldiethyl amine mixtures at 35° and 47°C., and from these has computed free energies, heats and entropies of mixing. The signs of the excess quantities ($F^E > 0$, $H^E < 0$, $S^E < 0$) are consistent with the lower consolute temperature (49.4°) found for this system.

Mathot, Staveley, Young & Parsonage (49) have studied liquid mixture methane-carbon monoxide at 90.67°K., the triple point of methane. The observed excess free energy (28 cal./mole at $x = 1/2$) and the observed volume contraction (-0.32 cm.^{3}/mole at $x = 1/2$) are in good agreement with the predictions of the cell theory of Prigogine & Mathot (7).

Barthel & Dodé (50) have used radioactive methods to measure partial vapor pressure above the system carbon tetrachloride-bromine at 0°C. From their data, one can calculate an excess free energy of mixing of 112 cal./mole at $x = 1/2$, in reasonable agreement with the difference in solubility parameters ($\Delta\delta = 2.9$).

Phibbs (51) has measured ΔH and ΔV for the process of mixing glutaronitrile with each of a large series of solvents, mostly polar. When correlating this with the solubilities of tetracyanoheptane and polyacrylonitrile, it was found that the good solvents were those characterized by both evolution of heat and volume expansion upon mixing.

Gorbachev & Kudryashov (52) have measured partial vapor pressures above mixtures of toluene and 2,2,4-trimethyl pentane over a range of temperatures; from their data, one may calculate F^E to be about -35 cal. at 20°C. and $x = 1/2$.

Brown & Smith (53) have investigated solutions of acetonitrile with benzene and with nitromethane. At 45° and $x = 1/2$, $F^E = 161$ cal./mole for the former system; at 60°C. the acetonitrile-nitromethane system is ideal within experimental error.

Thermodynamic information, particularly free energy data, may be deduced from vapor-liquid equilibrium measurements. Some of the systems studied, together with the approximate excess free energies (in cal./mole at $x = 1/2$) were: methylethyl ketone-carbon tetrachloride, 61 [Fowler & Norris (54)]; *n*-octane-ethyl benzene, 40 [Yang & van Winkle (55)]; methylcyclohexane-toluene, 75 [Weber (56)]; carbon tetrachloride-furfuraldehyde, 260 [Wingard *et al.* (57)]; BrF_3-BrF_5, 78 [Long (58)]; argon-oxygen, 11 [Fastovskii & Petrovskii (59)].

Taylor & Rowlinson (60) have investigated the thermodynamic properties of aqueous solutions of glucose, measuring vapor pressures, heats of dilution and solution, heat capacities, and densities. The excess thermodynamic functions are calculated and compared with those of sucrose solutions.

Heats of mixing.—One of the most interesting advances during the past few years has been the development of experimental techniques for accurate calorimetric measurement of the heat of mixing small quantities of two non-electrolyte liquids. Only a few years ago most of the heats of mixing reported in the literature were obtained from vapor pressure measurements at

a series of temperatures and were inevitably less accurate than the corresponding free energy values. Now heats of mixing are easily obtainable and to an accuracy greater than that of most free energy calculations. During the year, new calorimeters were described and a large number of new measurements reported; Table I summarizes these.

Most of these heats are small in magnitude, and it is not surprising that there is little or no correlation with solubility parameters, or indeed with any other theory. What Canning & Cheesman (61) say about the systems they studied is applicable to many of the others: "In the present state of our knowledge of molecular interaction it is not possible to make any predictions about such values except to foresee their smallness." The values Brown, Mathieson & Thynne (62) report for benzene-cyclohexane and benzene-heptane are well in excess of the values estimated from solubility parameters; these discrepancies are the only ones large enough to worry about.

TABLE I

CALORIMETRIC HEATS OF MIXING

System	Temp. °C.	ΔH^M (cal/mole at $x=1/2$)	Observer
benzene-cyclohexane	20	200	Brown, Mathieson, & Thynne (62)
benzene-*n*-heptane	20	230	Brown, Mathieson, & Thynne (62)
cyclohexane-*n*-heptane	20	67	Brown, Mathieson, & Thynne (62)
benzene-toluene	24.3	16.0	Canning & Cheesman (61) Cheesman & Ladner (63)
benzene-*p*-xylene	24.4	4	Cheesman & Ladner (63)
toluene-*n*-xylene	24.4	41	Cheesman & Ladner (63)
benzene-chlorobenzene	24.3	− 1.7	Canning & Cheesman (61)
benzene-bromobenzene	24.3	6.8	Canning & Cheesman (61)
chlorobenzene-bromobenzene	24.3	4.9	Canning & Cheesman (61)
toluene-chlorobenzene	24.3	−25.5	Canning & Cheesman (61)
toluene-bromobenzene	24.3	−18.9	Canning & Cheesman (61)
carbon tetrachloride-neopentane	0	75	Englert-Chwoles (11)
benzene-1,2-dichloroethane	25	15.2	Ruiter (65)
ethanol-carbon tetrachloride	45	135	Brown & Fock (66)
ethanol-2,2,4-trimethylpentane	25	150	Brown & Fock (66)
ethanol-benzene	45	280	Brown & Fock (66)

Cheesman & Ladner (63) have modified the calorimeter of Cheesman & Whitaker (64) so as to make accurate measurements of ΔH on 5 ml. samples

of liquid over a wide range of temperatures. The heat of mixing for the systems benzene-toluene, toluene-*p*-xylene, and benzene-*p*-xylene decreases almost linearly with temperature. If the Guggenheim interchange or local free energy w is defined as F^E/x_1x_2, these measurements, combined with free energy measurements, yield w, dw/dT, and d^2w/dT^2. (The parameter w is sometimes erroneously defined as H^E/x_1x_2, and the two uses should not be confused.)

Ruiter (65) has made precise measurements on the system benzene-1,2-dichloroethane at 7.6, 25.0, and 41.8°C. using a calorimeter of conventional design and a large 350 ml. sample. ΔH decreases with increasing temperature and is quite asymmetric on a mole fraction diagram.

Fluorocarbon solutions.—Mixtures of hydrocarbons with fluorocarbons continue to give outstanding examples of an inadequacy of solubility parameter theory; the heats and excess free energies of mixing of such systems are invariably much higher than predicted, and as a consequence, solubilities are very much lower than expected. The year 1955 has seen additional data, at least one new interpretation, and strong evidence to support an old interpretation.

Reed (67) has suggested that the large energies of mixing in hydrocarbon-fluorocarbon systems are due in part to (a) failure of the solubility parameter theory to take account of the large volume expansions on mixing (the energy of mixing at constant volume would be much smaller), and in part to (b) the failure of the geometric mean assumption, $\epsilon_{12}=(\epsilon_{11}\,\epsilon_{22})^{1/2}$. In the London theory of dispersion forces, the attraction constant k_{12} is proportional to the geometric mean of the polarizabilities of the molecular species and to the harmonic mean of the ionization potentials:

$$k_{12} = \frac{3\alpha_1\alpha_2 I_1 I_2}{2(I_1 + I_2)} \qquad 6.$$

In defense of the use of the over-all geometric mean, it is usually argued that the percentage variation in I is much less than that in α; a large difference between I_1 and I_2 would undoubtedly upset this. The ionization potentials of hydrocarbons lie in the range 10–13 e.v., and on the basis of a crude theoretical treatment (68), Reed estimates ionization potentials for fluorocarbons from 16–18 e.v. Such a large difference, coupled with the volume effect, will account fairly satisfactorily for the previously measured energies of mixing in the systems C_5F_{12}-C_5H_{12} and C_4F_{10}-C_4H_{10}. Analysis of more fluorocarbon-hydrocarbon systems and direct measurements of fluorocarbon ionization potentials will be needed to confirm this suggestion. One will also need to account for the fact that other substances (e.g. CCl_4) with ionization potentials close to those of the hydrocarbons behave so differently with fluorocarbons.

That fluorocarbons should have high ionization potentials is consistent with their high transparency in the vacuum ultraviolet (no band above 2100 Å). Evans (69) has emphasized the importance of perfluoroheptane as

a spectroscopic solvent and has found that solvent shifts (relative to the gas phase) are much less in it than in *n*-heptane.

Neff & Hickman (70) have measured total pressures over binary liquid mixtures of C_7F_{16} with *n*-heptane and 3-methyl heptane, $TiCl_4$ with heptane, and CCl_4 with 3-methyl heptane. They found they could bring their results in reasonable agreement with the predictions of Eqn. 3 only by arbitrarily increasing the solubility parameters of the hydrocarbons by about 0.8 to 1.1 units. This is in accord with an earlier suggestion by Hildebrand (71), but what makes these measurements especially interesting is the fact that $TiCl_4$ and CCl_4 have δ-values above those of the hydrocarbons, while that of C_7F_{16} is of course far below. Unless the hydrocarbon δ's are shifted upwards, one calculates for the solutions with the fluorocarbons much smaller deviations from ideality than observed; and for the other solutions much larger deviations than observed. This is one more piece of evidence against the now largely abandoned "interpenetration" model advanced by Simons & Dunlap (72); it would have predicted that the observed deviations would always have been larger than those estimated from solubility parameters.

More recently Hickman (73) has determined liquid-liquid phase diagrams for perfluoroheptane with four of the five isomeric hexanes. The critical solution temperatures are in the order of increasing solubility parameters (-0.5°C. with 2,2-dimethyl butane, $\delta_{25°C.} = 6.71$, to 28.5°C. with *n*-hexane, $\delta_{25°C.} = 7.27$), but are of course much higher than would be predicted by these thermodyanmic δ's. Here again an empirical shift offers a solution; if the solubility parameters of all the hydrocarbons are increased, this time by 1.7 units, excellent agreement is obtained.

Clegg & Rowlinson (74) have studied liquid-vapor equilibrium in the system sulfur hexafluoride-propane (chosen because the substances have almost identical molecular volumes) in the temperature range 25–70°C. and at pressures of 35–50 atmospheres; large positive deviations from ideality were observed.

Thorp & Scott (75) have measured total vapor pressures in the systems CF_4-CH_4, CF_4-Kr, CH_4-Kr in the region of 110°K. The solubility parameters of all three are similar, but only the last proves to be a nearly ideal solution; CF_4 is not far from unmixing with krypton and with methane at these temperatures.

Glew (76) has found the partial molar volume of iodine in perfluoroheptane to be 100 cm.^{3}, much expanded over the extrapolated molar volume of liquid iodine at 25°C., 59 cm. Scott (77) has shown this large volume change to be consistent with the very large activity coefficient (1400) of iodine in this solvent.

Brackett, Dunlap & Biscoe (78) have suggested that the entropy of fluorocarbon-hydrocarbon mixtures is less than would be expected with such large volume expansions and find evidence for incomplete mixing (on a microscopic scale) in their measurements of the small angle x-ray scattering from the system isoöctane-perfluoroheptane.

Complexes and Compound Formation

A very large amount of work on the formation of molecular complexes and compounds in solution was reported in 1955, not all of which can be mentioned here. A number of important papers were presented and discussed at the Third International Conference on Coordination Congress in Amsterdam in April, the proceedings of which are about to be published (79). Mulliken (80) summarized our present understanding of donor-acceptor molecular complexes in solution, with particular reference to his own theories of the stability of these complexes and their charge transfer spectra.

Powell (81) summarized recent work on clathrate compounds, those unusual solid structures within which small molecules of a gaseous or liquid species are caged. Von Stackelberg (82) reported on the structure of inclusion compounds of water and of phenol. Van der Waals (83) outlined a simple and remarkably successful statistical thermodynamic theory of clathrate compounds. He assumed that the structure of the substrate cage was independent of the number of cages filled, and that a caged gas molecule interacts only with its substrate surrounding and not with similar molecules in adjacent cages; one is then led directly to a relation between the gas pressure and the fraction of cages occupied which is identical with the Langmuir equation for monolayer gas adsorption. The constants in the equation can be related to molecular parameters by using the cage theory originally applied to liquids by Lennard-Jones & Devonshire. Agreement of calculated thermodynamic quantities with those observed experimentally is altogether remarkable.

Högfeldt (84) presented his treatment, first published elsewhere (85) of compound formation in solution. If one assumes that the compound and the reactants from which it is formed mix ideally, all apparent deviations from ideality (i.e. referred to formal mole fractions of the components) are due to the failure to recognize the true molecular species. Total excess free energies are always negative but, except for the simplest AB complex, the partial molar quantities $\overline{F}^E$, and $\overline{F}_2^E$ (i.e. log γ_1 and log γ_2) can change sign at particular concentrations. Determination of these "cross-over" concentrations would permit estimation of the formula A_mB_n of the complex were it possible to exclude or allow for other sources of nonideal behavior.

Ginell & Shurgan (86) have refined the theory of linear association, but in applying it to mixtures of phenanthrene and ethanol draw the physically absurd conclusion that it is the phenanthrene (*not* the ethanol) which associates! Eppler (87) has measured ultrasonic absorption in a series of binary liquid mixtures; where one or both components are of the type usually regarded as "associating" (e.g. hydrogen-bonding liquids, etc.), special nonadditive effects are observed.

Hydrogen bonding.—It has long been assumed, in order to explain the thermodynamic and other properties of solutions of chloroform in solvents containing oxygen and nitrogen, that chloroform formed compounds in which the electropositive hydrogen formed a weak hydrogen bond with the

electronegative O or N. Huggins, Pimentel & Shoolery (88) have now studied the temperature and concentration dependence of the proton magnetic resonance of chloroform in acetone and triethylamine solutions, and have found strong confirmation for this view. Were the complex long-lived, one would expect two resonance frequencies, one for the proton in the complex, ν_z, and one for the proton in the free chloroform, ν_c. However, when as here, the lifetime of the complex is short compared with the time $1/(\nu_c - \nu_z)$ there is only one resonance whose frequency is an average weighted according to the relative proportions of free and complexed chloroform. From the variation at 28°C. of the observed resonance with concentration of chloroform, the authors deduce a mole fraction equilibrium constant $K_x = 1.8 \pm 0.6$ for acetone-chloroform and 3.0 ± 1.0 for acetone-triethylamine. Similar measurements at -23°C. were combined with these to yield very rough values for ΔH of compound formation of -2.5 and -4.0 kcal. respectively. Within the rather wide limits of experimental error, these values for acetone-chloroform agree with values used to fit the vapor-pressure data.

Huggins & Pimentel (89) had earlier tried to study the hydrogen bonding effect by infrared measurements of the C-D stretching frequency of deuterochloroform in various solvents. The usual correlation between frequency shift and strength of the hydrogen bond (as evidenced by heats of solution) was not observed. A correlation between integrated intensity of the vibrational band and the strength of the interaction was observed. A similar study of hydrogen bonding of deuterochloroform was made by Lord, Nolan & Stidham (90). They measured the frequency shifts and intensities of the C-D stretching vibration of chloroform in a somewhat different set of solvents, and found qualitatively similar results. From careful quantitative measurements of the intensity of this vibrational band in a series of mixtures of chloroform in diethyl ether, the authors calculate an equilibrium constant of 0.80 ± 0.15 liters/mole; this corresponds to 60 per cent of the chloroform complexed in an equimolar mixture, somewhat greater than that calculated from vapor-pressure data. Bernstein & Tamres (91) have reported additional data on the solvent shift of the C-H and C-D stretch in chloroform, pentachloroethane, and the corresponding deuterated species. Carbon disulfide and a perfluoroether produce small shifts in opposite directions, which may be related to the fact that these solvents lie at opposite ends of the solubility parameter spectrum.

Vinogradov & Linnell (92) have found that pyridine and pyrrole react together to form a 1:1 complex, as evidenced by infrared absorption, calorimetric measurements, and other physical properties; they report the ΔH of formation as -3.8 kcal. Pyrrole itself is associated, which fact makes simple thermodynamic calculations difficult. McDonald, Gibbs, & Ladd (93) have studied the infrared spectrum of benzyl alcohol in dilute solution in three solvents, toluene, benzyl fluoride, and anisole. The fact that the spectrum, particularly that due to the O-H stretching frequency, is essentially the same in benzyl fluoride as in toluene, leads the authors to conclude that there is

no hydrogen bonding between the OH and the F; a weak hydrogen bond to the anisole is indicated.

Hydrogen bonding in phenol-solvent systems has been investigated by Tsubomura (94) using infrared techniques. Equilibrium constants for the formation of a complex between phenol and a proton acceptor solvent range from about 9 liters/mole with ethylether and acetonitrile to about 110 liters/mole with hexamethylene tetramine; measurements at three temperatures yield a ΔH of -6.9 kcal. for the formation of the phenolhexamethylene tetramine complex. Vidale (95) has made a Raman spectroscopic investigation of the molecular complexes of dimethyl ether with hydrogen chloride and with hydrogen bromide; he finds evidence for both hydrogen bonding complexes and ion pair complexes.

Weinberg & Zimmerman (96) have measured the proton magnetic resonance of the hydroxyl hydrogens in water-ethanol mixtures. In solutions rich in ethanol, two distinct resonances are observed, but between 40 and 50 mole per cent water, this coalesces to a single line. This behavior is interpreted as meaning rapid proton exchange, with an average lifetime of approximately 0.05 second, in these water-rich mixtures.

Denyer, *et al.* (97) have used measurements of the partition of trimethylamine between vapor phase and solution to calculate equilibrium constants for the formation of complexes between the amine and a series of solvents, mostly ones capable of hydrogen bonding. The strongest complexes observed were those with *p*-chlorophenol and β-naphthol, with K about 200 liters/mole.

Schellman (98) has analyzed existing data on solutions of urea in water on the basis of a theory of association of urea molecules. From the data he deduces an association constant $K_2 = 4.1 \times 10^{-2}$ l./mole and a $\Delta H = -2.09$ kcal.

Electron donor-acceptor complexes.—Collin & D'Or (99, 100) have observed an infrared absorption by a freshly prepared solution of chlorine in benzene which they attribute to the charge transfer complex. This absorption at 526 cm.$^{-1}$, well displaced from the 557 cm.$^{-1}$ fundamental of chlorine (which is also observed), has an intensity and polarization which leads the authors to conclude that the chlorine molecule in the complex is not parallel to the benzene plane and must be oriented in a nonsymmetrical way with respect to that plane. Mulliken (101) has briefly commented on this interpretation, in general agreeing with it. It is difficult, however, to reconcile this observation with the low "acidity" of chlorine; this halogen is a far poorer acceptor than bromine and iodine, and one would expect its complex with benzene to have too low a concentration to be observed.

Keefer & Andrews (102) have determined a full set of thermodynamic constants (ΔF, ΔH, ΔS) for the formation of donor-acceptor complexes of polyalkylbenzenes with iodine in carbon tetrachloride solution and Ogimachi, Andrews & Keefer (103) have reported similar data with iodine monochloride as the acceptor. Except for the relatively greater strength of the

ICl complexes, the two series yield comparable results; ΔS and ΔH both increase regularly with increasing ΔF, and both series fall on the same straight line. Anomalously low K's (attributed to steric hindrance) are found for hexaethylbenzene, pentaethylbenzene, and for tri-t-butyl benzene; these anomalies show up in both ΔH and ΔS, and these complexes still fall on the inter-relating line.

Kortüm & Vogel (104) have measured the solubility of iodine in mixtures of cyclohexane and various aromatic hydrocarbons. Large increases in solubility in the mixture over that inferred from the solubilities in the pure components are attributed to formation of the charge-transfer complex. Equilibrium constants are deduced, and the solvents placed on a basicity scale ranging from chlorobenzene (very weak) to 2,3,6-trimethyl naphthalene (strong); the results agree qualitatively with those of other workers.

Evans (105) has found that the ultraviolet absorption spectrum of iodine in perfluoroheptane and in diperfluorohexyl ether is indistinguishable from that of gaseous iodine. There is, however, a strong absorption in the region of 220 to 260 mμ for solutions of iodine in paraffin hydrocarbons, an effect present to a much smaller extent when chloroform is the solvent. The interaction of iodine with n-heptane was studied quantitatively; the usual Benesi-Hildebrand plots give an intercept near the origin which may be interpreted as meaning an equilibrium constant of approximately zero. The author concludes that this absorption is not a solvent shift of the N-V transition of iodine but the charge transfer transition of a very weak, possible "collisional," complex. Evans also reports (106) similar results with analogous interpretations for bromine solutions.

Another kind of "collision" complex was reported by Ketelaar & Hooge (107); they found in the infrared absorption spectra of liquid solutions of bromine in carbon disulfide lines whose frequencies are the sum of two fundamentals, one for each molecule. The authors interpret these lines as due to the absorption of electromagnetic radiation at the moment of collision, causing simultaneous vibrational transitions in both molecules; similar phenomena have been observed in compressed gases [Coulon, Robin & Vodar (108)].

Corkill, Foster & Hammick (109) have determined the equilibrium constants for formation of the benzene-1,3,5-trinitrobenzene and benzene-chloranil complexes in cyclohexane solution (0.77 and 0.65 l./mole, respectively); their new method consists of observing spectrophotometrically the competition for the Lewis acid between benzene and various aniline bases.

Bier (110) reported at Amsterdam on measurements of thermodynamic constants for the formation of complexes with organic nitro compounds in solution. He found large variations in the ΔH of formation but a relatively constant value for ΔS, in contrast to the results which Keefer *et al.* obtained for systems with halogen acceptors.

Castro & Andrews (111) have measured equilibrium constants (in CCl_4 solution) for the formation of donor-acceptor complexes between methyl

substituted biphenyls and 1,3,5-trinitrobenzene; K is sharply decreased by even a single ortho substituent and is practically zero for bimesityl. Apparently when one ring is forced out of coplanarity with the other, it forces the acceptor trinitrobenzene molecule out of a favorable position for interaction; either the parallel orientation or the 3 Å ring separation is lost.

Bayliss & Brackenridge (112) have measured the perturbation of the ultraviolet spectrum of nitromethane in a series of mixed solvents: benzene-heptane, benzene-dioxane, benzene-carbon tetrachloride, toluene-carbon tetrachloride, dioxane-heptane, toluene-isoöctane, dioxane-methanol, toluene-methanol, and dioxane-water. The first five can be interpreted in terms of weak complexes (the Benesi-Hildebrand equation yields small K's), but the authors point out that they can equally well be interpreted as a physical perturbation of the solute molecules by the solute environment. The results for the remaining mixed solvents could be interpreted as involving the formation of somewhat stronger complexes, but Bayliss and Brackenridge prefer to talk about a physical perturbation which reaches saturation with one active solvent molecule in the nearest neighbor shell. They believe that this strong saturated physical perturbation can be distinguished from a chemical complex by determining whether in a pure active solvent, there are one or two solute species present; however, this would appear to depend on the lifetime of the species as compared with the time of measurement.

Scott (113) has discussed the Benesi-Hildebrand method of evaluating the equilibrium constant K and extinction coefficient ϵ of complexes from spectrophotometric data; uncertainty about nonideal behavior of the solutions presents an unresolvable ambiguity in the constants reported.

Phase Equilibria

Liquid-liquid solubilities.—The ozone-oxygen system has been studied by Brown, Berger & Hersh (114) and by Jenkins, DiPaolo & Birdsall (115), with results which are in essential agreement. Below a critical solution temperature of 93°K., the two liquids are only partially miscible; as would be expected from the difference in molecular size, oxygen is more soluble in the ozone-rich phase than vice versa.

Vol'nov (116) has determined the mutual miscibilities at low temperatures of silicon tetrachloride with ethanol, *n*-propanol, malonic ester and acetoacetic ester. Tsiklis & Vasil'ev (117) have studied phase separation of argon-ammonia mixtures at temperatures between 70° and 140°C.; while both substances are gaseous under normal conditions, the homogeneous phase separates at high pressures (up to 6800 kg./cm.^{2}) into two with all the characteristics of liquid-liquid phase separation. Similar behavior has been observed by Tsiklis *et al.* (118) in the system hydrogen-propane at high pressures. Mironov (119) has measured the liquid-liquid phase diagram of diethyl ether with hydrogen peroxide; the critical solution temperature is 46°C.

Ferguson (120) has noted that the solubility in water of diethyl ether

and higher ethers is very similar to the solubility of the isomeric normal alcohol and finds this hard to reconcile with the prevailing view that the great differences in water solubility between ethanol and propanol and their isomeric ethers is due to the great capacity of the former for hydrogen bonding; special steric effects are suggested.

Leland, McKetta & Kobe (121) have measured the mutual solubilities of 1-butene and water at pressures up to 700 atm. They have also re-examined the problem of calculating the solubility of water in hydrocarbons; the geometric mean assumption for ϵ_{12} is not very satisfactory, but the authors suggest an empirical relation which gives good agreement with the data for water in methane, ethane, propane, and *n*-butane.

Solubility of gases in liquids.—Peter & Weinert (122) have measured the solubility of H_2, CO, CO_2, and H_2O vapor in liquid hydrocarbon fractions (of average molecular weight 250–350) in the region of 200°C. The solubility of hydrogen and carbon monoxide are unexceptional, but the solubilities of carbon dioxide and of water vapor increase with temperature, corresponding to a negative ΔH of solution.

McKinnis (123) has developed an empirical treatment of the solubility of acetylene in donor solvents; his equation involves bond orders, electronegativity differences, bond distances, and other effects, good agreement between predicted and observed solubilities (with an average deviation of less than 10 per cent) is claimed.

Smith (124) has measured the solubility of chlorine gas in carbon tetrachloride between 40° and 90°C.; the experimental line is parallel to that for the ideal solubility and also parallel to the solubility in dibromoethane measured by Gjaldbaek & Hildebrand (125); the "cross-over" inferred by extrapolating older data does not exist.

Lachowicz, Newitt & Weale (126) have measured the solubilities of hydrogen and deuterium in *n*-heptane and *n*-octane at 25°, 37.5°, and 50°C. and a range of pressures. Within experimental error (about 1 per cent), the solubility increases with increasing temperature. In another paper Lachowicz (127) has discussed relative solubilities of H_2 and D_2 at low temperatures (e.g., below 100°K.); deuterium should have a slightly higher extrapolated vapor pressure, a smaller molar volume, and a higher solubility parameter, all effects which should increase its solubility over that of hydrogen.

Solubility of solids.—Doane and Drickamer (128) have investigated the effect of pressure on the solubility of phenanthrene, anthracene, stannic iodide, and hexachloroethane in carbon disulfide and a series of aliphatic hydrocarbon solvents. Pressures as high as 10,000 atm. were used, and the solubilities were found to decrease regularly with increasing pressure. The authors interpret their data by calculating how the solubility parameter of the solute must increase with increasing pressure if agreement with the Scatchard-Hildebrand-Flory-Huggins equation is to be maintained; a more straightforward thermodynamic approach would involve partial molar volumes.

Hoerr *et al.* (129) have determined the solubility of three long chain methylalkyl ketones (2-nonanone, 2-tridecanone, and 2-nonadecanone) in a variety of solvents; chloroform is a good solvent, but acetone is not. Qualitative agreement with the solubility parameter scale is found, but not much significance should be attributed to δ-values for substances like CH_3OH and CH_3CN even though they fit here.

Ward & Singleton (130) have measured the solubility of 1-monostearin in several polar and one nonpolar solvent.

Ewald (131) has reported measurements on the solubility of solid xenon and solid carbon dioxide in compressed nitrogen, hydrogen and helium. The solubility of Xe in N_2 and in H_2 is in agreement with values calculated from data on the pure components using the usual combining rules for virial coefficients. He suggests that the anomalously low solubility of the solids in helium is due to solid solution formation, and that the abnormally large solubility of carbon dioxide in hydrogen is due to a CO_2-H_2 interaction stronger than a geometric mean would give.

Mauser & Kortüm (132) have discussed the theory of solubilities of gases and solids in liquids, and have shown how the partition of a solid solute between two immiscible liquids can be calculated from data on solid solubilities. They have measured the distribution of iodine between water and carbon disulfide; they find slight deviations from constancy of the distribution factor, deviations which are in excellent agreement with their calculations.

Solid solutions.—Heastie (133) has measured the solid-liquid phase diagram for argon-krypton mixtures; this belongs to Roozeboom's Type I, but its shape suggests positive deviations from ideality in the solid solution phase greater in magnitude than the positive deviations in the liquid phase. No evidence of separation into two solid phases was found in measurements extending as low as 62°K.; Domb (134) has reported calculations which suggest a critical solution temperature in the region 10–40°K.

Sackmann (135) has reexamined the system CCl_4-CBr_4 and finds that the solid solution region extends only from 0 to 20 per cent CBr_4, in disagreement with previous work which reported complete miscibility of the two components in the solid state. Kofler (136) has reexamined the solid-liquid equilibrium for phenanthrene-anthracene mixtures; extensive solid solutions do exist, but miscibility is not complete. and the system is Type IV (a peritectic diagram).

Miscellaneous

Viscosity of solutions.—Several new attempts to correlate the viscosity of binary mixtures with the thermodynamic properties of the solutions have been made. Reik (137) found good agreement for some systems with an empirical equation involving the viscosities of the pure components and the cube roots of the activity coefficients. Vándor (138) derived an equation for the viscosity of strictly regular solutions; his correction to the usual logarithmic relation uses the quasi-chemical equation to calculate deviations from randomness; why this minor refinement should be added is not clear. Hill

(139) has found fair agreement between experimental data and a theory relating diffusion coefficients with viscosities in binary mixtures.

Surface tension of solutions.—Teĭtel'baum & Osipov (140) have measured the surface tension of nitrobenzene-hexane mixtures over a wide range of temperatures; the surface tension of both pure components decreases linearly with increasing temperature, but those of 20–30 per cent hexane solutions are almost independent of temperature between 0 and 50°C. The bulk properties of the solution show no peculiarities in this region; so the authors suggest the unusual surface properties are due to surface demixing. Saroléa-Mathot (141) has treated theoretically the surface tension of solutions of molecules of differing size; she finds that the Flory-Huggins method yields high results because it overestimates the entropy decrease when the surface is formed.

Metallic solutions.—Fiorani, Valenti & Genta (142, 143, 144, 145) have investigated the thermodynamic properties of several binary liquid metal systems (Zn-Ga, Zn-Sn, Ga-Zn) and one ternary system (Zn-Cd-Sn). Kleppa (146) has determined calorimetrically the heats of mixing of several liquid metal systems (Bi-Pb, Cd-Pb, Cd-Sn, and Sn-Zn) and finds the results in good agreement with values obtained from EMF measurements. Sanbongi & Ohtani (147) have studied three liquid alloys of iron (Fe-Mn, Fe-Ni, and Fe-Co), and find all three to be approximately ideal. Other metallic systems for which thermodynamic measurements were reported are Ag-Au [Zhukovitskii *et al.* (148)], Ag-Mg [Kachi (149)], Ag-Zn [Trzebiatowski & Terpilowski (150)], Cu-Ni [Rastogi & Varma (151)], and Cu-Pt [Assayag (152)].

Booth & Rowlinson (153) have modified the statistical theory of order-disorder transitions of alloys to allow for the energy of thermal vibration of the atoms in the lattice. Inclusion of this effect increases the heat capacity at the λ-temperature, as Linder (154) had observed earlier, but the calculated values still fall short of those observed (e.g., for β-brass).

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STATISTICAL MECHANICS[1]

By John E. Kilpatrick

Department of Chemistry, The Rice Institute, Houston, Texas

During recent years a strong tendency to reexamine critically the basic assumptions of quantum statistical mechanics has been evident. The relatively new field of quantum-statistical treatment of non-equilibrium phenomena has also shown great activity, while many older topics, such as the nature of the condensation process, the melting process, and properties of solid solutions, are perhaps more active today than they have been for many years. New methods, both analytical and numerical, are being developed for the treatment of the liquid phase. Hope seems to be justified that we shall soon be able to handle liquids as well as we now can handle real gases.

Fundamentals.—An excellent discussion of some basic points in statistical mechanics has been given by ter Haar (1). He is particularly concerned with the relations between (and the basis of) the H-theorem and the ergodic theorem, both in classical and in quantum statistics. His comprehensive bibliography covers the most important fundamental papers in the subject.

Watanabe (2) has written an interesting series of three papers on the general quantum- and statistical-mechanical consequences of the space-time symmetry of physical laws. In the first paper he is mainly concerned with the various forms of the principle of detailed balance. The second paper is devoted to field theory while in the third paper of the series, the various aspects of "prediction" and "retrodiction" are discussed. This latter subject, of course, is the very heart of the still incompletely settled question of the precise relation of the time-reversible microscopic equations and the irreversible macroscopic equations. The crux of Watanabe's argument seems to be that, although equal a priori weights assigned to the various quantum states is plausible enough in prediction, the situation is quite different in ordinary retrodiction. He argues that the usual assumption that equal weights are equally applicable to extrapolations from a given initial state in both directions in time and that therefore Boltzman's H-theorem is symmetric in time is equivalent to nothing more that the simple statement: information about a system decreases in both directions in time as we extrapolate from a given state of the system.

The use of perturbation theory in quantum statistics has been discussed by Nakajima (3). This powerful technique enables one to deduce series expansions for the various thermodynamic functions in which the higher moments of the perturbation appear as coefficients. The partition function may be written in the several equivalent forms:

[1] The survey of the literature pertaining to this review was concluded in January, 1956.

$$Z = \exp(-\beta F) = \sum_n \exp(-\beta E_n) = \text{trace}(\exp[-\beta H]) = \sum_n \langle \psi_n, \exp(-\beta H)\psi_n \rangle$$

where F is the Helmholtz free energy, $\beta = 1/kT$, the E_n are the eigenvalues of the Hamiltonian H and the ψ_n a complete set of orthonormal functions not necessarily eigenfunctions of H. The Hamiltonian is expressed as

$$H = H^0 + \epsilon H'$$

where ϵ is small and H^0 is simple enough that the direct evaluation of the partition function offers no problem.

In one approach, due essentially to Kubo (4), the density operator $R(\beta) = \exp(-\beta H)$ is expressed in the symbolic integral representation

$$R(\beta) = \frac{1}{2\pi i} \oint \frac{\exp(-\beta H)}{E - H}\, dE.$$

Since the poles of the argument lie on the real axis at the eigenvalues of H, the contour must enclose this axis counterclockwise. If now $(E-H)^{-1}$ is replaced by the identity

$$\frac{1}{E-H} = \frac{1}{E-H^0} + \frac{1}{E-H^0}\epsilon H' \frac{1}{E-H^0} + \frac{1}{E-H^0}\epsilon H' \frac{1}{E-H^0}\epsilon H' \frac{1}{E-H^0} + \cdots$$

one can obtain the elements of the density matrix using the zeroth-order wave functions as a basis:

$$\begin{aligned}\langle m|\, R(\beta)\,|\, n\rangle = {} & \delta_{mn} f_1(E_n^0) + \epsilon \langle m|\, H'\,|\, n\rangle f_2(E_m^0, E_n^0) \\ & + \epsilon^2 \sum_r \langle m|\, H'\,|\, r\rangle \langle r|\, H'\,|\, n\rangle f_3(E_m^0, E_r^0, E_n^0) + \cdots\end{aligned}$$

where

$$f_\nu(E_\alpha^0, E_\beta^0, \cdots) = \frac{1}{2\pi i} \oint \frac{\exp(-\beta E)}{(E - E_\alpha^0)(E - E_\beta^0)\cdots}\, dE.$$

The f integrals are readily evaluated:

$$f_1(E_\alpha^0) = \exp[-\beta E_\alpha^0]$$
$$f_2(E_\alpha^0, E_\beta^0) = [f_1(E_\alpha^0) - f_1(E_\beta^0)]/(E_\alpha^0 - E_\beta^0), \text{ etc.}$$

It is of particular interest that no difficulty arises in the evaluation of any of the f's when two or more arguments are equal, in contrast to the complications that occur in the degenerate case of ordinary quantum mechanics. One can now write the partition function of the perturbed ensemble as the trace of this expansion of the density matrix:

$$\begin{aligned}Z = {} & \sum_n f_1(E_n^0) - \epsilon \sum_n \beta \langle n|\, H'\,|\, n\rangle f_1(E_n^0) \\ & - \frac{1}{2}\epsilon^2 \sum_m \sum_n \beta\, |\langle m|\langle H'|\, n\rangle|^2 f_2(E_m^0, E_n^0) - \cdots.\end{aligned}$$

In the foregoing formalism, the correction terms appear as matrix elements of H' over the zeroth order wave functions. Alternatively, averages over the unperturbed canonical ensemble may be introduced by the definition

$$\langle Q\rangle \equiv \text{trace } (\exp\,[-\beta H^0]Q)/\text{trace } (\exp\,[-\beta H^0]).$$

With the aid of the operator

$$H'(\lambda) \equiv \exp\,[\lambda H^0]H' \exp\,[-\lambda H^0]$$

the density matrix may be written in the form of an integral equation

$$R(\beta) = \exp\,[-\beta H^0]\left\{1 - \epsilon\int_0^\beta d\lambda H'(\lambda)\exp\,[-\lambda H^0]R(\lambda)\right\}.$$

This equation may be solved by iteration and after some manipulation we obtain

$$Z = Z^0\left\{1 - \epsilon\beta\langle H'\rangle + \frac{1}{2}\epsilon^2\int_0^\beta d\lambda\langle H'(\lambda)H'\rangle + \cdots\right\}.$$

Nakajima gives several illustrative applications of these equations.

Landsberg (5) has continued and extended the discussion begun by Thomsen (6) concerning the relations between some of the fundamental concepts and theorems of statistical mechanics. The main content of Thomsen's discussion is summarized in Prigogine's (7) review.

Relations between ensembles.—Lax (8) has examined the relation of averages calculated in canonical and microcanonical ensembles. He states that the results are equivalent providing the microcanonical calculation can be evaluated by a steepest descent method; otherwise incorrect results may be obtained in the canonical calculation. The exact basis of the classifications "correct" and "incorrect" is not clear inasmuch as the two ensembles correspond to somewhat different physical models. Ansbacher and Landsberg (9) have extended and completed their arguments (10), that for the two cases: an ideal B. E. gas and an ideal F. D. gas, the exact mean quantum state occupation numbers calculated from a canonical ensemble and a grand canonical ensemble become equal in the limit of an infinite system of finite, non-zero density. It seems likely this result will be found to hold in general.

Hill (11) and Katsura (12) have discussed the question of whether or not an S-loop should be expected in p versus V/N (or in μ versus N/V) in the condensation region of a real gas, using the canonical ensemble. In other words, does a canonical ensemble of a real gas lead to a retrograde region in the p-V isotherm (as in the van der Waal's equation) or is there a two-phase flat? Van Hove (13) has shown that no loop is obtained from a complete evaluation of the canonical partition function of an infinite fluid. Hill (14) has shown that a grand canonical ensemble can never lead to a loop. It would be surprising and of considerable interest if an exact treatment of the canonical ensemble, in the limit $N\to\infty$, N/V finite, did not lead to the same results as obtained from the grand canonical ensemble. Hill and Katsura agree that certain approximate treatments of the canonical ensemble lead to a van der Waals loop. Katsura gives an argument that would appear to extend his results in the case of a finite lattice gas to include the case of an infinite fluid. Hill points out that one approximation in Katsura's treatment, neglect of interfacial energy, can be shown to be just enough to force the

formation of two phases. Siegert (15) has shown earlier that consideration of the very small interactions between the large cells of van Hove's model leads to the same results.

Gases.—In the last few years there has been some interest shown in the role that clusters play in the equation of state of real gases (16, 17, 18). It is, of course, not necessary to introduce clusters explicitly into a statistical mechanical derivation of the virial equation. With the aid of the grand partition function written in terms of the partition functions for one, two, etc., molecules in a container of volume V, all of the virial coefficients may readily be expressed as functions of these canonical partition functions. The second virial coefficient, for example, is given by

$$B = -N_0V(Z_2 - \tfrac{1}{2}Z_1^2)/Z_1^2$$

where Z_2 and Z_1 are the partition functions for two and one, respectively, molecules in a container of volume V and temperature T. N_0 is either unity or Avogadro's number according to whether the molecular or the molar second virial coefficient is desired. There is nothing about Z_2 that implies the formation or absence of binary clusters, i.e., a definite bonding or association of two molecules to form a unit. On the contrary, Z_2 is summed over all states of the two atoms, both those that would normally be identified with two separate molecules and those associated with two "clustered" molecules.

On the other hand, it is sometimes desirable or is of interest to introduce the properties of explicit clusters into the analysis. For example, Wooley (17) following Mayer's (19) example, defined his clusters as independent and then proceeded to deduce expressions for the virial coefficients in terms of equilibrium constants of formation of the clusters from the free molecules. One disconcerting result of this treatment is that at temperatures high enough for the second virial coefficient to become positive, the concentration of binary clusters and their equilibrium constant of formation become negative. Similar results are found for larger clusters and one is led to the ridiculous conclusion that the total number of clusters may be larger than the number of molecules in the system.

This paradox has been very neatly and elegantly resolved by Hill (20). The root of the paradox is in the assumption that the clusters can be defined so that they are all independent. In the usual derivation of the virial equation, one writes the grand partition function as

$$\Xi = \sum_{N=0}^{\infty} Z_N z^N$$

where $z = \exp(\mu/kT)$ and obtains p/kT as a power series in $\rho = \overline{N}_0/V$,

$$p/kT = \sum_{n=1} \alpha_n \rho^n$$

by eliminating z between the equations

$$pV/kT = \ln \Xi$$

$$\overline{N}_0 = z \frac{\partial}{\partial z} \ln \Xi.$$

Hill writes the grand partition function as

$$\Xi = \sum_{\mathbf{N}} Z_{\mathbf{N}} \prod_s z_s^{N_s},$$

where $\mathbf{N}$ is a set of non-negative integers $N_1, N_2, N_3, \cdots$ and z_s is the absolute activity of a cluster of s molecules. The partial partition functions $Z_{\mathbf{N}}$ are related by the equations

$$Z_1 = Z_1$$
$$Z_2 = Z_{20} + Z_{01}$$
$$Z_3 = Z_{300} + Z_{110} + Z_{001}, \text{ etc.}$$

The quantity $Z_{n_1 n_2 \cdots}$ $(= Z_{\mathbf{N}})$ is defined as the sum of the terms (or the integral on the region of phase space) of Z_N, $N = \sum s n_s$, that is identified with n_1 single molecules, n_2 binary clusters, etc. Now with the use of the equation for the average (equilibrium) number of s-clusters

$$\bar{n}_s = z_s \frac{\partial}{\partial z_s} \ln \Xi$$

followed by the condition of equilibrium between clusters

$$z_s = z_1^s = z^s$$

the density of s-clusters, $\rho_s = \bar{n}_s / V$, may be found as a power series in ρ, the total density.

Up to this point no assumption as to independence of clusters has been introduced. Hill has merely implied that, if we are to talk about clusters as such, we must make up our minds clearly as to the prescription for deciding which of the states of a system of N atoms (or what regions of the phase space of N atoms) shall be identified with a given partitioning of the N atoms into clusters. If this can be done realistically and unambiguously, the cluster argument will make sense; otherwise the results are confusing and probably physically meaningless even though mathematically correct. A prime example of the latter case is a system of nonattracting billiard balls, where no real clustering occurs.

The Mayer assumption of cluster independence may now be introduced by the equation

$$p/kT = \rho_1 + \rho_2 + \rho_3 + \cdots$$

which leads to the virial expansion

$$p/kT = \rho - \frac{V Z_{01}}{Z_1^2} \rho^2 - \cdots.$$

Comparison of this result with the previous equations for the second virial coefficient in terms of Z_2 leads to an interesting conclusion that Hill does not draw, namely that

$$Z_{20} = \tfrac{1}{2} Z_1^2.$$

That is to say, the cluster independence hypothesis is the whole prescription for subdividing Z_2 and turns out to be at least a partial prescription for the

higher partition functions. Now for a gas with a positive second virial coefficient

$$Z_2 = Z_{20} + Z_{01} < \tfrac{1}{2}Z_1^2$$

and therefore Z_{20} is larger than Z_2. In other words, we are assigning more than all of the phase space of two molecules to the two separate molecules configuration and less than no volume to the configuration of one cluster of two molecules. It is remarkable how this consequence of Mayer's very plausible hypothesis is subtly buried in the canonical ensemble approach and how glaringly obvious it becomes in the grand canonical approach.

Siegert (21) has calculated the number density probability function $W(N)$ of a two-dimensional Yang and Lee lattice gas on a toroidal surface with a finite number of sites. He finds that $W(N)$ has at least two sharp maxima and therefore this finite gas should not have a continuous, S-loop, liquid-vapor transition. See also Hill (11) and Katsura (21).

Shimose (22) has approximated the equation of state of a two dimensional lattice gas which appears to show both a sharp solid-liquid transition and a more diffuse liquid-vapor transition. He uses a billiard-ball, square well potential with a repulsive radius equal to a and an attractive radius of $\sqrt{2}a$. The molecules are allowed at the sites of a square array of spacing a/n, with $n=2$, 3 or 4. The density ρ is so defined that the perfect crystal with atoms at the sites with spacing a has a density of unity. The liquid-vapor critical densities for the above three cases are $\rho_c=0.377$, 0.352 and 0.344, at the critical temperatures $\epsilon/kT_c=1.979$, 1.794, and 2.013. The explanation of this somewhat erratic behavior of the critical temperature is not obvious.

Kihara (23, 24) has continued his work on the second and third virial coefficients of pure gases and of mixtures. He has deduced the expression for $B^{(3)}$, the third quantum correction to the medium temperature, asymptotic expansion of the second virial coefficient in powers of $\hbar^2/2\mu$ together with the first quantum correction to the third virial coefficient. These corrections are explicitly evaluated for the Lennard-Jones 12-6 and 9-6 potentials. He has fitted the experimental data on the second virial coefficient of He^4 (range 14°K to 423°K) to his equations and obtained some new potential constants:

r_0	ϵ/k	
3.11A	7.82°K	9,6 potential
2.88A	10.80°K	12,6 potential

The latter set give a somewhat deeper well than do those of de Boer & Michels (25). Kihara argues that he has proved that the two body He^4 system definitely has a discrete level but we do not find his reasons absolutely conclusive. A variety of different simple analytic potentials, (26, 27, 28, 29) some with and some without discrete levels, fit the very low, medium, and high temperature second virial coefficient data for He^4. What these potentials have in common is that they are all very close to the situation of having a discrete level right at zero energy. It would seem that we would have to

have experimental data about one order of magnitude better than we have, or alternatively, a good quantum mechanical calculation of the potential, in order to really settle the question. Arguments based on the third virial are confused by the probable non-additivity of the pair potentials.

There has been some speculation as to whether the phenomenon of condensation might not be related to divergence of the virial expansion. Such a relation would not seem likely in that neither the pressure nor the density virial expansion is the more fundamental. It would be surprising if both series have the same radius of convergence. Indeed, very little has been done with the question of convergence of the virial equation of state of any substance. In at least one special case, the density expansion of an ideal Bose-Einstein gas, it has now been shown that the radius of convergence is finite but well past the condensation point.

The virial problem is neatly formulated in Widom's (30) notation. The reduced density and pressure.

$$x_1 = \rho(h^2/2\pi mkT)^{3/2}$$
$$x_2 = (p/kT)(h^2/2\pi mkT)^{3/2}$$

are two cases of the generalized zeta function defined by

$$x_s = \sum_{n=1}^{\infty} n^{-(s+1/2)} z^n$$

where $z = \exp(\mu/kT)$. The momentum cluster integrals are the coefficients $n^{-3/2}$. The density virial expansion is obtained by eliminating z between the equation for x_1 and x_2:

$$x_2 = x_1\left[1 + \sum_{1}^{\infty} \alpha_n x_1^n\right].$$

The α_n are reduced virial coefficients. Widom (30) finds an explicit determinant of order n in the cluster integrals for the α_n. This result is exactly equivalent to the one given by Kilpatrick (31) in an expanded form, as may readily be seen from the discussion of recurrence in Muir (32).

The Bose-Einstein condensation point occurs at $x_1 = \zeta(3/2) = 2.612 \cdots$. Widom was able to show that the virial series has a radius of convergence $R \geqq \frac{1}{2} \exp(2/3) = 0.257 \cdots$ and conjectured that the radius is infinite. Shapiro (33) shows that the radius is actually finite. Fuchs (34) has completely finished the problem. He shows that

$$12.56 \approx 4\pi \leqq R \leqq \zeta(3/2) + 4\pi \approx 27.73.$$

The radius of convergence is definitely finite but is much larger than 2.612, the Bose-Einstein condensation point. There would now seem to be little point in determining the precise radius of convergence; however, the behavior of the virial series in the neighborhood of the condensation point might throw some light on the analogous problem in real gas condensation.

Liquids.—Barker (35) has discussed the several approximations involved in the cell theory of liquids (see Lennard-Jones & Devonshire (36), Kirkwood

(37), Mayer & Careri (38), and de Boer (39)). These are (1) communal effects, the reduction of the entropy due to the restriction of single cell occupancy, (2) correlation effects, the second order effects of the actual simultaneous motion of the molecules as opposed to the assumed motion of each molecule in a fixed potential field, (3) the smearing approximation, the assumed angular independence of the potential in each cell. Barker makes estimates of the magnitude of each of these approximations and considers how the current theory may be improved.

De Boer's (39) cell-cluster theory for liquids has been continued by Cohen, de Boer & Salsburg (40). The two major difficulties in the application of this method are (1) the calculation of the configurational partition function of multiple cell clusters occupied by more than one molecule, (2) the evaluation of a combinatorial weighting factor involved in the partitioning of the molecules among the cells. In the last quoted reference a good approximation for this factor is deduced for binary clusters by a method similar to that used by Kikuchi (56, 57) in order-disorder problems in crystals. The results of this paper are applied to the ideal gas in order to show that a large part of the missing communal entropy of the single cell Lennard-Jones treatment appears when only binary clusters are included in the calculation. The binary configurational partition function has been calculated for some simple cases (hard spheres; harmonic forces) by Salsburg (41).

Rowlinson & Sutton (42) have treated the thermodynamic properties of a liquid whose bimolecular potential can be expressed as the sum of a Lennard-Jones type potential and a non-spherical, orienting term. In a later paper, these authors (42) have also studied two-component solutions.

Alder, Frankel & Lewinson (43) have used the Monte Carlo technique to calculate the radial distribution function for hard spheres. Their low density (up to 20 per cent of closest packing) results agree with those found from the superposition principle. Qualitatively their curves agree with those found by the Rosenbluths (44). A detailed comparison is difficult due to the fact that the two groups did not use exactly the same densities in their several calculations. By the use of the superposition principle Alder (45) has calculated the radial distribution function of a binary mixture of hard spheres of different diameters.

Liquid Helium.—The second-order lambda transition of liquid helium is similar in some respects and dissimilar in other respects to the first order liquid-vapor transition of a classical fluid. Perhaps the greatest point of similarity is in the cluster description of both transitions. The lambda point clusters, however, for an ideal Bose-Einstein gas are wholly in the momentum coordinates of phase space, rather than in the space coordinates. Real He^4 has, of course, a weak long-range attractive potential between molecules together with a short range repulsive core. The actual clustering that might be expected would be in all dimensions of phase space to some degree but probably much closer to pure momentum clustering than to pure space clustering.

For an ideal Bose-Einstein gas, it is found that the lambda point is first-order under constant volume but third order under constant pressure. Chester (46) has continued his earlier work in which an ideal Bose-Einstein helium is perturbed with weak intermolecular forces and has now shown that very small forces can change both the constant volume and constant pressure lambda transitions into second order transitions. With the use of a fairly plausible potential rather good quantitative agreement is found with the experimental lambda region heat capacity. The most unrealistic part of his calculation is the deletion of the hard core repulsion. This is undoubtedly connected with the decidedly poorer results obtained above the lambda point. On the whole, however, his results are a decided improvement over those from the ideal gas model. In a later paper, Chester (46) has distinctly improved upon Kikuchi's (47) treatment of Feynman's (48) model. Chester is able to show that, lacking the advent of some rather improbable contingencies, Feynman's model does exhibit a second order lambda point.

Butler & Friedman (49) have developed a relatively simple expression for the partition function of an assembly of interacting Bose-Einstein particles. They calculate the heat capacity of liquid helium at constant volume around the lambda point and find results intermediate between those observed experimentally and those calculated for an ideal Bose-Einstein gas. Morita (50) has discussed the hydrodynamics of the "phonon gas" in He II with the aid of cell theory. He concludes that sharp pulses are propagated as second sound above 0.5°K. but not below this temperature.

Butler, Blatt & Schafrath (51, 52) in a series of papers discuss the superfluidity of an ideal Bose-Einstein gas, the moment of inertia of a rotating fluid, and the equilibrium versus non-equilibrium nature of superfluid helium. These authors contend they have established that at true thermodynamic equilibrium no superfluid can exist and that therefore helium II must be in some long-lasting metastable state. Their arguments, however, seem to be more nearly objections to the roton-phonon or the two-fluid models than to actual He II.

Feynman's (48) method for handling the quantum statistics of cooperative systems has been applied with some success by Kikuchi (53) to liquid He^3. He^3 presents a considerably more difficult problem for this method than does He^4, due to the nuclear spin and to the fact that Fermi statistics make certain of Feynman's approximations more dubious. The calculated nuclear magnetic susceptibility agrees very well with the experimental results. Observing that the specific heat of liquid He^3 can be empirically fitted by a combination of Einstein and Debye functions, Temperley (54) is led to consider a cell model of this substance. He assumes each cell has only a few discrete, well defined, one-particle energy levels and that the higher energy states are multiparticle levels, smeared out into a Debye continuum.

Crystals.—Hijmans & de Boer (55), in a series of papers, have reformulated and developed into a consistent, unified method Kikuchi's (56, 57) lattice figure system of treating the Ising lattice. In their approach, the

proper equations for any level of approximation can readily be deduced. Rushbrooke & Scoins (58) have also studied the two-component Ising lattice. They focus their attention on the irreducible cluster sums (which are quite analogous to the cluster integrals of gas theory.) It develops that the simple ideal solution treatment and the quasi-chemical approximation are the natural zeroth and first order solutions in this approach.

Potts & Ward (59) have applied the algebraic method of Onsager (60) and Kaufman (61), and Kaufman and Onsager (62) to calculate the exact partition function of the two-dimensional toroidal Ising lattice, both for a finite and for an infinite number of sites. Potts (63) has also used the combinational Kac & Ward (64) method to obtain the partition function of the two dimensional plane triangular lattice.

Random walks and long chain molecules.—The statistical-mechanical calculation of the physical properties of a long-chain linear flexible polymer usually requires certain information about the various moments of the molecule. Of particular interest is the mean square length $\langle r^2 \rangle$ as a function of the length of the chain. This calculation, of course, may be formulated as a restricted random walk problem, with restrictions depending upon the nature of the relation between successive links of the chain and upon the physical requirement that no two atoms or groups in the chain may occupy the same region of space. A great deal of effort has been expended in attempting to solve this problem analytically, with somewhat inconclusive results. The restriction prohibiting chain crossing (ring closure) is particularly difficult to handle analytically.

Several groups have now applied Monte Carlo (random sampling) procedures to various particular cases of this problem and have accumulated a large body of interesting experimental information. With the initial member of the chain as an origin, a lattice of sites is assumed corresponding to all possible locations of subsequent members of the chain. The first link of the chain is defined by the orientation of the lattice. The second (and subsequent) members of the chain are chosen in a random fashion from the small finite number of possibilities until finally some version of the anti-chain-closure rule is encountered.

Wall, Hiller & Wheeler (65), Rosenbluth & Rosenbluth (66), and Wall, Hiller, & Atchison (67) have studied a number of simple two- and three-dimensional lattices. Wall and co-workers continued each chain with a random choice for the orientation of each new link until a crossing occurred. An extremely large number of trials was necessary to obtain an appreciable number of long chains. It was found that the probability of generating a chain of n links varied as a negative exponential function of n. The Rosenbluths used a more complicated but more efficient system. The random choices for the position of each new link were restricted to just those that would not result in a double occupancy of a site. In this system it was necessary to associate with each chain a weighting factor so defined as to take into account the number of choices available to each new link:

$$W_0 = 1$$
$$W_n = (i/N)W_{n-1}$$

where W_n is the weight associated with a chain of n links, N is the number of orientations normally open for a link, and i is the number of choices not involving a double occupancy open to the nth link. A chain therefore never terminated until i reached zero. This weighting system, of course, has the effect of requiring that a larger (but properly weighted) sample be drawn from the small but very important region of phase space associated with long chains. Such devices should be used more often in Monte Carlo calculations in order to improve the quality of samples possible with present day computers.

Both Wall *et al* (65) and the Rosenbluths (66) found that the mean square lengths of their chains could be represented by

$$\langle r^2 \rangle = an^b$$

with $b \sim 1.45$ for plane lattices and $b \sim 1.22$ for three-dimensional lattices. This form is consistent with the observed behavior of viscosity with molecular weight.

Irreversible processes.—Several paths have now been developed for the derivation of the well known Onsager reciprocal relations between the coefficients of the phenomenological equations that describe irreversible processes. The present situation is concisely discussed in a paper by de Groot & van Kampen (68). In Onsager's (69) original derivation some results regarding fluctuations are deduced and are used in finding the reciprocal relations. Casimir (70) has extended the derivation to include not only simple scalar phenomena but also vectorial and more general tensorial processes. De Groot & Mazur (71) have avoided the integral equations used by Casimir in favor of using differential equations leading to the same results. Van Kampen (72) has deduced Onsager's scalar reciprocal relations from quantum statistics. De Groot & van Kampen (68) have extended this method to get Onsager's fluctuation results and to deduce the general tensorial reciprocal relations directly from the scalar relations. These extended relations have been applied to a number of transport processes. Kluitenberg & de Groot (73) have deduced a relativistic form of the second law of thermodynamics properly invariant with respect to tensorial terms such as electric polarization and magnetization.

Popov (74) deduces the Onsager reciprocal relations by assuming that the entropy change in the approach to equilibrium can be given by an expression of the form

$$-2\Delta S = \sum \sum g_{ij} x_i x_j + O(x_i^3)$$

where the x_i are displacement variables from the equilibrium states and the cubic and higher ordered terms may be neglected. This treatment would seem to be formally equivalent to the usual approach to the reciprocal relations.

Bergman & Lebowitz (75) have begun to investigate the properties of an apparently useful model in the description of irreversible processes. The system interacts with a set of infinite heat reservoirs by means of impulses. In this initial paper only temperature gradients in the system are considered. The ensemble obeys an integro-differential equation in phase space, containing the terms of the Liouville equation and a kernel that describes the collisions or impulses with the reservoirs. The ensemble is shown to approach a canonical distribution in the presence of one driving reservoir or to approach a steady temperature gradient state in the presence of several reservoirs and in the latter case, to satisfy Onsager's reciprocal relations. These authors have assumed some fairly strong microscopic reversibility conditions and it remains to be seen whether these assumptions are really necessary. The impulse nature of interaction with the driving reservoirs which has been assumed seems particularly reasonable on physical grounds.

Eisenschitz (76) has applied a virial theorem to the relation between ensemble averages. In this way he has directly deduced expressions for the flux of energy and of momentum in a rather general assembly. His expression for the momentum flux agrees with that deduced by Falkenhagen (77), Born & Green (78), and Irving & Kirkwood (79). His expression for the energy flux differs somewhat from the several expressions given by the above authors. Eisenschitz contends that these differences are due to the fact that Born & Green (78) and Irving & Kirkwood (79) introduced a plausible but arbitrary conjecture in passing from the divergence of the energy flux to the energy flux itself.

Van Hove (81) has given a new derivation of the differential equation

$$\dot{P}_\alpha = \sum_\beta (W_{\alpha\beta}P_\beta - W_{\beta\alpha}P_\alpha)$$

which describes the approach to equilibrium of an ensemble not too far away from equilibrium. His method avoids the repeated use of the random phase assumption (or its classical analogue, molecular chaos). For two classes of initial states, namely (1) where the absolute amplitudes of the unperturbed states vary slowly over an energy range $\hbar/\tau_0$ (where τ_0 is the time of relaxation in the approach to equilibrium) and (2) where the spread of the unperturbed energy states is small compared to $\hbar/\tau_0$, no random phase assumption is needed at all. The key to van Hove's treatment is the following observation: In most cases of interest, certain matrices, related to the perturbation operator that is responsible for the approach to equilibrium, have δ-type singularities in their diagonal terms in the limit of an infinite number of degrees of freedom in the ensemble.

Lloyd and Pake (82) have raised the question of whether the principle of detailed balance necessarily holds in a nonequilibrium system. Klein, (83) using a simple three energy state system, shows that cyclic processes like

$$1 \rightarrow 2 \rightarrow 3 \rightarrow 1$$

must occur in a steady state due to forced $1 \rightarrow 2$ transitions and that therefore detailed balance does not hold.

Biot (84) has developed a general theory of irreversible processes for systems close to equilibrium. He finds that the principle of minimum entropy production holds, not only in a steady state condition, but in the approach to a steady state. His principal tool is a variational principle and he makes a number of applications of his methods to problems in viscoelasticity. Prigogine and Balescu (85) have considered the conditions under which one may deduce a rate potential governing the approach to equilibrium. This potential is always non-increasing and takes a minimum value in the steady state. In the neighborhood of equilibrium it becomes the rate of entropy production.

Green & ter Haar (86) have continued their discussion of statistical fluctuations in the approach to equilibrium. Prigogine & Mayer (87) have related the theorem of minimum entropy production to the probability of fluctuations about a steady state. They have shown that the satisfying of this theorem is a necessary condition for the application of the Einstein fluctuation formula.

Certain ambiguities arise in the choice of phenomenological coefficients when all of the fluxes and conjugate forces in a non-equilibrium system are not independent. Hooyman & de Groot (88) have shown that in this event the coefficients may be chosen in such a way as to satisfy the Onsager relations.

Waelbroeck, Lafleur & Prigogine (80) have considered the effect on the thermal conductivity of a gas due to the transport of the "heat of association" of the molecular clusters.

General—An interesting theory of a ferromagnetic spin system has been developed by van Kranendonk (89). In this treatment certain approximations in the usual spin-wave approach are by-passed by developing a formal spin-deviation gas whose properties can then be expanded into a virial series as in the case of any real gas.

Prigogine & Bingen (90) have continued Prigogine and Klein's (91) study of the time dependence of the distribution functions of chains of harmonic oscillators. The same local ergodicity, in spite of the non-ergodicity of the system as a whole, is found in three dimensional chains as was found in one dimensional assemblies.

Hart & Guier (92) have treated a two-dimensional system of weakly interacting particles which execute quasi-periodic motion in a Newtonian potential field. The radial mass distribution function for a system having the same energy and momentum per unit mass as the solar system bears a surprisingly close resemblance to the actual mass distribution of the planets.

Harris & Alder (93) have discussed the assumptions and approximations involved in a derivation of the Onsager equation for dielectric polarization. These authors have previously given a statistical derivation (94) for this quantity which in the limiting case of short-range forces only reduces to an

equation given by Piekara & Zakrzewski (95). On the other hand, Kirkwood (96) and Fröhlich (97) have given equations which in the same limiting case reduce to the Onsager equation. The discrepancy is a factor which is usually close to unity, at least in the range of validity of the Kirkwood model. Harris and Alder show that their model is actually more general than the Kirkwood-Fröhlich model and that the two limiting formula are the same after all when equivalent simplifying assumptions are made in both derivations.

A new text-book in quantum-statistical mechanics has been published by Band (98). There are a number of attractive features of this book, in particular, a fair selection of recent applications of statistical mechanics are discussed. The treatment of the relations between the various ensembles, however, is a little brief, as is the basic development given of the grand ensemble.

Ecker (99) has discussed in considerable detail the fundamental processes involved in a statistical treatment of assemblies involving strong interaction between particles. He is particularly concerned with the range of validity of the individual particle description of collisions.

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RADIATION CHEMISTRY[1]

By C. J. Hochanadel and S. C. Lind

Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee

Introduction

This review summarizes the work of the past year in the field of radiation chemistry. Greatest emphasis is placed on those studies which appear to have aided most in the understanding of the mechanisms by which chemical changes are produced by the absorption of high energy radiations. A review of radiation chemistry for the previous year was published by Dainton (1), and of both radiation chemistry and hot atom chemistry by Willard (2). Also, the review by Krauss, Wahrhaftig & Eyring (3) entitled "Mass Spectra and the Chemical Species Produced by the Impact of Low Energy Electrons" discusses an important phase of the radiation chemistry of gases. Other review articles were by Tolbert & Lemmon (4) on pure organic compounds, by Heal (5,6) on solids, and by Allen (7) on water and aqueous solutions. Included in the recent literature on radiation chemistry are the following books: the second edition of *Actions of Radiations on Living Cells* by Lea (8); *Fundamentals of Radiobiology* by Bacq & Alexander (9), which includes chapters on physical principles, indirect action, aqueous systems, and macromolecules; *Chemical and Biological Actions of Radiations*, edited by Haissinsky (10), which includes chapters by Gray on physical aspects, by Lefort on chemical aspects, and by Dale on biochemical aspects; *Collection of Papers on Radiation Chemistry*, edited by Bach (11), and a chapter on physical principles underlying radiation chemical reactions by Franck & Platzman (12). Also of interest to the radiation chemist are the monograph *Hydrogen Peroxide* by Schumb, Satterfield, & Wentworth (13), which includes discussion of mechanisms of the various reactions of hydrogen peroxide, an important product in the radiolysis of aqueous systems, and the book by Laidler entitled *The Chemical Kinetics of Excited States* (14). Accounts of discussions held at Paris (15, 16) on liquids, at Notre Dame (17) on water and aqueous solutions, and at the Radiation Research Society meeting in New York (18, 19) have been published. A symposium on radiation effects on polymers was included in the American Chemical Society Meeting in Cincinnati (20). Discussions of radiation effects in atomic reactors, and also of the uses of reactor radiations to promote desired chemical reactions were included in the International Conference on the Peaceful Uses of Atomic Energy at Geneva (21), and at the Nuclear Engineering and Science Congress at Cleveland (22). Accounts (11, 21, 23) of research carried out in Russia in recent years were made available to the world for the first time during the past year.

[1] The literature survey for this review was concluded in January, 1956.

Gases

The radiation chemistry of gases was in its earlier development largely confined to the effects of α-rays on account of their greater absorption. Recent researches are extended to β- and γ-radiation which are reported in the present review. The high sources of Co^{60} γ's and the ease of their introduction into high pressure gases has given impetus to these researches which have practical as well as theoretical importance. Also the availability of tritium opens a new avenue for the application of weak β-rays to the induction of gas reactions.

The decomposition of CO_2 by α-rays was investigated by Harteck & Dondes (24) using Rn from $RaCO_3$. At room temperature they found practically no decomposition of CO_2, confirming the earlier results of Wourtzel (25), and of Lind & Bardwell (26). This they attribute to rapid back reaction of chain type. Two means of inhibiting the back reaction promote decomposition: low temperature and small concentrations of NO_2. At 77°K. solid CO_2 with radon slowly evolved 2 $CO+O_2$, confirmed by recombination. The rate, a few μm. per hour became slower with time. No. O_3 was found. The formation of $CO+O_2$ in the presence of NO_2 was somewhat faster, nearly 4 mm. in 25 hr., independent of the concentration of NO_2 (3.8 and 6.3 per cent). Some suboxide of C was found at the low temperature, none in the presence of NO_2. The ion yield $-M_{CO_2}/N=3$ to 3.5 was calculated from pressure change by Pirani gauge and ionization from saturation current. In the Brookhaven reactor at 140°C., NO_2 (0.5 per cent) was used to suppress the back reaction. Assuming the decomposition of CO_2 mainly attributable to γ-radiation (10 per cent of the total energy), it is estimated that 8.5 per cent of the CO_2 should have been decomposed during the exposure; experimentally 8.1 per cent was found. This conversion of 25 per cent of the radiative energy to chemical reaction is the largest transformation of this kind known. A striking result is that solid CO_2 under α-radiation at 77°K. decomposes to CO and O_2 with the high yield $G=9$ to 10.

The polymerization of organic unsaturates by α's of Rn was confirmed by Professor Mund (see 27). Isobutene was examined at O°C. and constant pressures (40 to 69.5 cm. Hg). One mole of H_2 is liberated for 2 moles of isobutene polymerized, corresponding to a mechanism: $C_4H_8^+ + e \rightarrow C_4H_7 + H$ and $H + C_4H_8 \rightarrow C_4H_7 + H_2$. Two molecules of polymer are formed per ion pair. The molecular weight of the polymer was determined cryoscopically in cyclohexane (constant 202):

TABLE I

Molecular Weight of Polymer in Cyclohexane

	I	II	III
Molecular Wt.	429.7	410.6	739.4
Polymerization factor	7.673	7.332	13.203
Millicuries Rn (initial)	50.56	22.79	74.54

The authors attribute the lower molecular weights of Experiments I and II to incomplete removal of unpolymerized C_4H_8 from the polymer before determining the molecular weight.

The equilibrium at 20°C., $H_2+D_2 \rightleftharpoons 2HD$, determined by Thompson & Schaeffer (28) with Po-210 α's and 2 mev electrons was compared with that in Ni catalysis. The exposures extended over 25 half-times disclosed equilibrium identical with the Ni catalytic value. Probably no discrepancy exists between the theoretical and β-ray equilibrium in the case of $T_2+H_2 \rightleftharpoons 2HT$ (29).

Crystalline α-ray acetylene reaction products were detected (30) by electron microscopy (12,000×, 37,500×). The source was 6.7 mc. Rn, in a thin α-ray bulb within the reaction vessel filled with C_2H_2 at 35 mm. pressure. The solid product deposited on Ni screens was examined as deposited without manipulation. The appearance of crystals leaves unexplained their absence in his former product made by radon mixed with C_2H_2 (31, 32, 33).

Mme. Lormeau-Loustau (34) studied the emission of ultraviolet light (1900 to 2600) under α-irradiation of N_2, O_2, H_2, and the mixtures of N_2-O_2, N_2-H_2, and H_2-O_2. The emission from H_2-O_2 mixture was the sum of that of the two components, while emission from mixtures of N_2-O_2 and N_2-H_2 was less than additive. Nonadditive effect was thought to indicate chemical reaction, which is known to occur between N_2 and O_2 or H_2 under α-radiation. No explanation could be offered for additivity in O_2-H_2, where the yield of chemical reaction is much higher than in the other two cases.

The ion-pair yield of the reaction between oxygen and tritium induced by the tritium β-radiation was determined by Dorfman & Hemmer (35) at 25°C. in a spherical pyrex bulb (212 cc.) using a Bourdon gauge to measure pressure. The initial reaction rate of H_2 and O_2 is proportional to the concentration of tritium resulting from its β-intensity and independent of the O_2 concentration attributable to the short range of the β-rays. The rate is slightly dependent on the ratio of H_2:T_2, tending to rise with increase of the proportion of protium. The initial rate, $R_o = 1.19 \times 10^{-4}\ C_{T_2}(1+0.3\ m_H)$ where C_{T_2} is the tritium in moles per liter and m_H is the mole fraction of protium in the mixture of hydrogen isotopes. $M_{T_2O}/N = 3.25$, close to that of water synthesis by α-radiation in H_2+O_2 (36) and in D_2+O_2 (37) reactions. Material balance measurements indicate that little or no H_2O_2 appears in the products, though it is probably formed in a chain terminating step such as $TO_2+TO_2=T_2O_2+O_2$.

Douglas (38), mixing T_2 with H_2 and CO, obtained a white solid polymer of formaldehyde resulting from the action of tritium β's on the $CO+H_2$ (T_2) mixture. The reaction was quite similar to that of α-rays (Rn) on $CO+H_2$ both in yield and nature of product. No methane was formed. The reaction products were measured by mass-spectrograph and included the various formaldehydes, >acetaldehydes, >glycols, to be expected in a mixture of CO, H_2, and T_2.

The reaction of acetylene under β-radiation of tritium was studied at ordinary temperatures by Dorfman & Shipko (39). Two products, cuprene

and benzene, were found. Benzene was captured in a cold finger at solid CO_2 temperature. 21 per cent of C_2H_2 trimerized to C_6H_6 (independent of C_2H_2 pressure and radiation intensity), confirming Rosenblum's (40) claims for α- and for β-γ-irradiation. The over-all yield for the disappearance of C_2H_2 ($-M_{C_2H_2}/N_{ions}=20$) agrees with early α-ray data (41). G values are: ($-G_{C2H2}=71.9$; $G_{C6H6}=5.1$). The use of C_2D_2 in some of the experiments showed that its ion yield is the same as that of C_2H_2, in agreement with the results for C_2D_2 under α-radiation (42). Dorfman & Shipko with Rosenblum (40) believe that benzene is formed by cyclisation initiated by excited C_2H_2 but adopt a mechanism for the formation of cuprene by polymerization initiated by free radicals (or possibly H atoms) and continued by the successive addition of C_2H_2. No mechanism for the termination of the chain at the critical value 20 is proposed. No disappearance of tritium nor exchange of tritium with C_2H_2 or C_2D_2 was observed, which is interpreted to mean that no significant dissociation of hydrogen isotope molecules occurs since the the reaction $T_2=2T$ would be expected to give $T+C_2H_2=C_2H_2T$ with loss of T_2 from the noncondensable fraction, which did not occur. However the exchange $C_2H_2+C_2D_2=2C_2HD$ does occur, but no HD appears in the noncondensable fraction.

In flame combustion of mixtures of propane and air and of ethylene with air at two intensities of β-radiation (Cu^{64} and Au^{198}) Cullen & Gluckstein (43) showed that the rate of combustion is greater at the higher source of radiation. No effect was observed with the lower sources, which eliminated the possibility of a spurious contact catalytic effect.

The energy (W) required to form ions in different gases has been experimentally compared for Po α- with that of β-rays by Jesse & Sadauskis (44). The ratio $W\alpha/W\beta$ is constant, and probably equal to 1, for H_2, He, Ne, A, Kr, and Xe, while for molecular gases, S_2, N_2, air, CO_2, CH_4, C_2H_4, C_2H_2, C_2H_6 ionization is higher (and W correspondingly lower) for β-rays than for α-rays. Betas of Ni^{63}, C^{14}, and of tritium gave identical results. The deviation of the ratio $W\alpha/W\beta$ results from a change of α- rather than of β-ionization.

Stevenson & Schissler (45) generated ions in a mass spectrograph and accelerated them toward a slit beyond which they collide and react: $X^+ + YH = XH^+ + Y$. The products were measured spectrographically. Exchange occurs on every collision; areas for reaction are about three times ordinary kinetic theory areas. The following specific reaction rates (independent of temperature) were found: (See Table II).

The rates are reproducible to ± 2 per cent; while systematic errors of calibration are believed to be less than 10 per cent. Eyring, Hirschfelder & Taylor (46) derived from the absolute theory of reaction rates both the correct form of the rate constant for such reactions and also the correct magnitude of the reaction $H_2^+ + H_2 = H_3^+ + H$.

Measurement of the appearance potentials of the ions AH^+ and KrH^+ proves that both are formed exclusively by the action of A^+ or Kr^+ ions with H_2 molecules.

TABLE II

RATES MEASURED IN MASS SPECTROGRAPH

Reaction	$K \times 10^9$ cm.^{3}/molecule sec.
$D_2^+ + D_2 = D_3^+ + D$	1.4
$A^+ + H_2 = AH^+ + H$	1.8
$A^+ + HD = AH^+ + D$	1.6
$A^+ + DH = AD^+ + H$	0.7
$A^+ + D_2 = AD^+ + D$	1.4
$CD_4^+ + CD_4 = CD_5^+ + CD_3$	1.3

The energy, W, to produce an ion pair by electron bombardment was measured by Weiss & Bernstein (47) in the following gases: air, 33.9 ev; N_2, 34.8; O_2, 30.9; CO_2, 32.6; A, 25.5; CH_4, 26.8; C_2H_4, 26.3 by comparison with air. The results agree with those of J. P. Jesse and of G. Failla.

Appearance potentials of various ions by electron impact on propyne and 2-butyne were measured by Coots & Anderson (48). For comparison they determined the potentials of $C_2H_2^+$ (11.4 ± 0.1 v.), C_2H^+ (17.8 ± 0.2 v.) and C_2^+ (23.3 ± 0.5 v.). Argon was used as reference ion. The results for ions from propyne were: $C_3H_4^+$ (10.3 ± 0.1 v.); $C_3H_3^+$ (11.8 ± 0.1); $C_3H_2^+$ (14.0 ± 0.1); C_3H^+ (18.4 ± 0.3); C_3^+ (26 ± 1); and for butyne: C_4H^{6+} (9.9 ± 0.1); $C_4H_5^+$ (12.2 ± 0.1); $C_4H_4^+$ (14.0 ± 0.1); $C_4H_3^+$ (15.1 ± 0.2); $C_4H_2^+$ (16.7 ± 0.3); $C_3H_3^+$ (11.4 ± 0.2); $C_2H_3^+$ (14.7 ± 0.2).

Pshezhetsky (49) finds that when liquid oxygen or liquid nitrogen-oxygen mixtures are irradiated with electrons about 15 molecules of ozone per 100 ev are formed. Nitrogen oxides are formed with $G = 1.5$. For 16 to 400 ev electrons the velocity of oxidation of N_2 is proportional to its ionization. Oxidation reactions are initiated by ionization of nitrogen, whereas processes of excitation and ionization of oxygen play no important role. In ozone formation oxygen excitation and formation of atoms are of primary importance.

Foner & Hudson (50) have produced the free radical HO_2 by electrical discharge in H_2O vapor over H_2O_2 through the reaction $H_2O_2 + OH \rightarrow HO_2 + H_2O + 30$ kcal. A small quantity of HO_2 is produced directly from H_2O_2 (with the discharge off). By measuring the ion intensities of HO_2^+, O_2^+, HO_2^+ from H_2O_2, and of A^+ as standard potential (15.77 ev), the ionization potential of HO_2 is 11.53 ± 0.1 ev, of O_2 12.15 ± 0.1 ev, the appearance potential of HO_2 from H_2O_2 15.41 ± 0.1 ev.

Groth & Oldenberg (51) analyzed the experiments of Groth (52) on the dissociation of N_2 by excited Kr′ (1200 Å) and compared them with the dissociation of H_2 by excited Hg′ (53). N atoms are produced by transfer of electronic energy of Kr′ into electronic energy of N_2 to a repulsive level leading directly to dissociation.

Burton & Magee (54) enounce a general principle of successive excitation

by low-energy electrons based on the so-called "sub-excitation electrons" of Platzman (55). They consider a species A with electronic states A′, A″, A‴ below a state A^n which decomposes rapidly compared with all the other processes. There is a finite possibility that state A^n will be reached and hence decomposition attained. For $n=2$ to 5, the number of inelastic collisions required for half decomposition is estimated to be 10 or less. The mechanism presented has a rate proportional to the electron concentration not to be confused with "cumulative ionization" in glow discharge proportional to the square of the electron concentration. The general principle above is applied to methane in electrical discharge (56).

Hayward (57) studied the polymerization of C_2H_4, by γ-rays (400 c. Co^{60}) at various pressures and temperatures up to 21 atms. and 400°F. Clear liquids or white waxy solids were produced with ion yields of 4 to 300, higher at higher temperatures. Strong inhibition by 0.02 per cent O_2 caused induction period until O_2 is consumed, giving products that do not catalyze the reaction. During induction a normal ion yield about 4 equals that under α-rays. O_2 consumption is about 0.04 per cent per megaroentgen.

The decomposition of gaseous HBr by x-rays was measured by Zubler *et al.* (58) both in HBr and in mixtures with large excess of A, Kr, or Xe. Ionization was determined by saturation current in each of the pure rare gases with correction for HBr. This obviated the difficulty of measuring saturation current in pure HBr. Complete transfer of charge, such as $A^+ + HBr \rightarrow A + HBr^+$, is assumed. A quencher (CH_4, C_2H_6, or C_3H_8) was added to suppress excitation in the ionization cell. Br_2 was separated at low temperatures (−196° and −120°) and measured in a Beckman DU spectrophotometer. The average M/N yields of decomposition were A-HBr, 4.7; Kr-HBr, 4.0; Xe-HBr, 4.7; HBr, 4.6; HBr-Xe, 5.2. The fractional deviations above 4 are attributed to excitation. The exchange of ionization from inert to reactant is so efficient in all three mixtures that it persists where the reactant is a low percentage of the mixture.

The fixation of nitrogen in the Argonne CP-3 reactor was determined by Primak & Fuchs (59) by enclosing metallic Ni in ampules of vitreous silica at about 40°C. in various gases. No attack on Ni in dry O_2, N_2, or air, in moist O_2 slight attack, in saturated moist air a Ni salt was formed: $Ni + 3H_2 + N_2 + 3O_2 \rightarrow Ni(NO_3)_2 \cdot 3H_2O$. The yield was calculated to be about 1 atom of N reacting per ion, reliable within a factor of 2. This yield agrees with $M_{acid}/N_{total} = 0.75$ found by Lind & Bardwell (60) for α's in dry N_2 and O_2. Other metals were attacked, Al, Co, Cu, and Pb which gave radioactive contamination.

A paper at Geneva by Wright *et al.* (61) treats the effect of pile radiation on heterogeneous systems of air or N_2 and water. Regarding the deleterious concentrations of HNO_3 in water from radiation, two practical questions arise: (*a*) is the rate of acid production so high as to govern the size of ion exchanger; (*b*) what are the relative productions of acid from air in the gas phase and in solution. (*b*) The gas phase of air can be made so small that the

total acid contribution from gas and liquid phases is so low as to permit the use of N_2 instead of He as coolant; (*a*) different ratios of air to water at different neutron fluxes showed that acid concentration both in air and N_2 rise in direct proportion to the gas/liquid ratio and to the flux so as to dictate the size of interchanger. The formation of NH_4^+ in N_2-H_2O system is low but rises slowly with increasing N_2/H_2O.

Further investigation of charge exchange and electron detachment has been made at University College, London, at ion energies from 3 to 40 kev by Stedeford and at ion energies 100 to 4000 kev by Hasted (62). Charge transfer cross-sections were measured for H^+, H_2^+, He^+, and H^- in the rare gases and in H_2. Excited states of ions must also be taken into account, as, e.g., $He^+ + Kr \rightarrow Kr^{+\prime}(^4P) + He$.

Dalgarno & Griffing (63) have analyzed in detail the energy loss of protons in the energy range 10 kev to 3 mev passing through H_2, using the Born approximation. Ionization, excitation, capture excitation, capture momentum loss constituting total proton stopping power are separately estimated; and for impact of neutral H, ionization (single and double), excitation (single and double) simultaneous excitation and ionization, and capture excitation. Losses from negative ion impact are also estimated.

Boudart & DuBois (64) examined the energy transfer between energy rich molecules and some foreign gases by means of the stabilization of fluorescence. The increase of fluorescence of β-napthylamine in the presence of D_2 and SF_6 at 186°C. were compared with the results of Neporent (65) using various foreign gases. He and $H_2(D_2)$ are poor stabilizers on account of their limited number of degrees of freedom. The rotational and vibrational states of hydrogen do not contribute to the excitation or de-excitation. Impacts with complex molecules are more effective because of their longer duration and the greater number of degrees of freedom for energy transfer. SF_6 on account of its stability and complexity is a highly effective stabilizer. Specific differences between different foreign gases are difficult to explain. No reason could be found for the high efficiency of ammonia.

Water and Aqueous Solutions

Primary Processes.—The decomposition of water by the absorption of fast charged particles is generally believed to result from the production of excited and ionized water molecules along the particle track. Following the initial act of energy absorption, little is definitely known about the sequence of events leading to the final observed products. It is generally assumed that the excited molecules and ions are transformed into the free radicals H and OH. The mechanism by which the radicals are produced from the ions is in doubt. The two prominent theories proposed by Samuel & Magee (66) and by Platzman (67) differ as to the fate of the electron ejected in the ionization act, and as a result lead to different mechanisms for radical production, and to different spatial distributions of radicals. Either theory is consistent with part of the experimental observations of the radiation chemistry of solutions,

most important of which are these: (*a*) H_2 and H_2O_2 are initially observed products of radiolysis, with the H_2O_2 yield usually greater than the H_2 yield; (*b*) these "molecular" yields depend upon the reactivity and concentration of solute; (*c*) intermediates which undergo reactions similar to those of H and OH radicals are also produced; (*d*) the ratio of "molecular" to radical yield increases with increasing linear energy transfer (LET) along the track of the particle. Magee (68) has extended his treatment of the radical diffusion model to include competition of solute-radical reaction with radical combination. He showed how the variation of molecular yields for different particles, and the effect of scavenger such as Br^- (see 69) on the molecular yield, can be brought into agreement with the theory by proper choice of parameters.

Both Fricke (70) and Schwarz (71) have also extended the Samuel-Magee theory to include the effect of a single solute. The calculations agree reasonably well with the experimental data on lowering of "molecular" yields by solutes.

Platzman (55) has called attention to the significant role which subexcitation electrons may play in radiation chemistry. These electrons, having energy less than the lowest electronic excitation potential E_0 of the medium, may produce effects in a minor constituent having excitation or ionization levels below E_0, to an extent far out of proportion to its concentration. The concept has been applied to explain in part the large effect of trace impurities in lowering the value W (energy per ion pair) for the rare gases. Weiss (72, 73) has also called attention to the importance of subexcitation electrons and excited molecules in radiolytic reactions.

An important experimental observation pertinent to the radiation chemistry of aqueous systems is that of Jortner & Stein (74) who claim to have demonstrated a stable bound state of the electron in H_2O, CH_3OH, and C_2H_5OH by reacting freshly distilled potassium with these media at temperatures near the freezing point.

Kinetics of reactions.—Many observations of the radiolysis of water and dilute aqueous solutions are consistent with the view that the earliest detectable products, following the initial act of energy absorption, include H atoms, OH radicals, H_2, and H_2O_2. The molecular products H_2 and H_2O_2 are thought to be produced in the tracks of the particles, probably by radical combination, or possibly in part by a molecular reaction involving excited water molecules. In this discussion the primary reaction will be written as

$$H_2O \sim\!\!\!\sim\!\!\!\sim\!\!\!\

ured by adding solutes which react with all the free radicals and thereby "protect" the molecular products from secondary reaction. Yields of the radicals have been evaluated by measuring the changes in suitable solutes which react quantitatively with the free radicals. The H atom usually acts as a reducing agent, the OH radical as an oxidizing agent, and the peroxide may act in either way. In the presence of oxygen the HO_2 radical is formed, and it may act either as an oxidizing agent or reducing agent. Molecular hydrogen usually does not react directly with solutes; the important reaction it undergoes is:

$$H_2 + OH \rightarrow H_2O + H$$

In many reactions the observed yield is independent of the solute concentration, and depends only on the yields of the intermediates. The yields listed in Table III were chosen from the work of many people and are considered to be the most representative at present.

TABLE III

YIELDS OF THE INTERMEDIATES IN THE RADIOLYSIS OF AQUEOUS SOLUTIONS BY GAMMA RAYS, HARD X-RAYS, OR FAST ELECTRONS

	0.8 N H_2SO_4	10^{-2} N H_2SO_4 to Neutral Solution
$G_P(H_2)$	0.40	0.45
$G_P(H_2O_2)$	0.80	0.80
$G_P(H)$	3.70	2.75
$G_P(OH)$	2.90	2.05

In some reactions two or more solutes may compete for the same intermediate. Also, the molecular H_2 and H_2O_2 may compete for the radical intermediates. The rates of these reactions have, in most cases, been satisfactorily described using rate equations based on a homogeneous distribution of intermediates, assuming that each solute reacts with a given intermediate in proportion to the concentration of the solute and to the rate constant for the reaction. The initial distribution of intermediates is certainly not homogeneous, and the application of the simplified kinetics may not be justifiable. From studies of solutions containing more than one solute, ratios of rate constants have been determined. A list of these ratios has been published (17).

Gray (75) discussed radiochemical yields in terms of linear energy transfer (LET) along the particle track. It is now well established that the yields of the intermediates vary with the type of radiation, with the ratio of yields of molecular products to free radicals ranging from about 0.2 for γ rays and fast electrons, ~0.3 for $H^3\beta^-$ particles, ~0.9 for α particles, to almost 1 for fission recoil particles.

A number of new studies of the radiolysis of water in the presence of the decomposition products H_2, H_2O_2, and O_2 have been made. Most of the results can be explained by the simple mechanism:

$$H_2O \xrightarrow{\text{WW}} H + OH + H_2 + H_2O_2 \qquad P$$
$$OH + H_2 \rightarrow H_2O + H \qquad 1.$$
$$H + H_2O_2 \rightarrow H_2O + OH \qquad 2.$$
$$OH + H_2O_2 \rightarrow H_2O + HO_2 \qquad 3.$$
$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad 4.$$
$$H + O_2 \rightarrow HO_2 \qquad 5$$

The removal of radicals almost exclusively by reaction 4 was applied to the radiolysis of these solutions by Allen (76) and was indicated by the work of Lea (77) on the photolysis of dilute solutions of H_2O_2. By bubbling H_2, O_2, or He (or N_2), either singly or in combination, through solution during radiolysis, either or both of reactions 1 and 5 can be eliminated, the concentrations of gases are maintained constant, and the kinetics are greatly simplified. Pure water and H_2O_2 solutions were studied at 25°C. by Ebert (78) and by Hochanadel & Davis (79) using the bubbling technique. Most of the results could be described by rate equations based on the above mechanism. The combination of H_2 and O_2 dissolved in water and irradiated with gamma rays at 200°C. and 250°C. could also be explained using the above mechanism provided the reaction $HO_2+H_2O_2 \rightarrow H_2O+O_2+OH$ was included in order to remove the H_2O_2 produced.

The gamma ray-induced exchange of deuterium gas with water was studied by Gordon & Hart (80). D_2 is converted to HD by the reactions $H+D_2 \rightarrow HD+D$, $OH+D_2 \rightarrow HOD+D$, and $D+D \rightarrow D_2$. The formation of HD was cited as evidence for formation of H atoms in the decomposition of water. The HD yield of about 3 showed a peculiar drop with pH in the range 2 to 9.

Gordon, Hart & McDonnell (81) studied the effect of deuterium substitution on the gamma-ray-induced reaction of hydrogen with hydrogen peroxide. The combinations studied were (*a*) $H_2+H_2O_2$ in H_2O; (*b*) $D_2+H_2O_2$ in H_2O; (*c*) $D_2+D_2O_2$ in D_2O (*d*) $H_2+D_2O_2$ in D_2O. The reaction proceeded as described previously (82) and rates were in the order $d>c>a>b$, from which it follows that $k(H_2+OH)>k(D_2+OH)$ and $k(H_2+OD)>k(D_2+OD)$.

In the gamma irradiation of extremely pure air saturated water, Allen & Holroyd (83) observed a peroxide yield of 1.23. They also found an effect of bromide ion at pH 5 similar to that reported by Sworski (69) for solutions at pH 2. From the mechanism previously proposed (69), the peroxide yield in aerated bromide solution is given by $G(H_2O_2)=G_P(H_2O_2)+\frac{1}{2}[G_P(H)-G_P(OH)]=2G_P(H_2O_2)-G_P(H_2)$. Using the value 0.45 for $G_P(H_2)$, the value for $G_P(H_2O_2)$ was 0.77 at pH 2 and 0.68 at pH 5. Using 140 kvp x-rays Mayneord *et al.* (84) obtained the high H_2O_2 yield of 1.83. Added Cl^- and Br^- produced decreases in yield, and benzene an increase in yield as expected. An observed increase in yield by F^- is difficult to explain.

Hart, Gordon & Hutchison reported further work (85) on the gamma irradiation of solution of $O^{16}O^{18}$ in H_2O^{16} in the pH range 0.4 to 9.65. Although

the results were somewhat erratic, the initial yields of products allowed estimates of the yields $G_P(H_2O_2)$, $G_P(H_2)$, $G_P(OH)$ and $G_P(H)$ to be made. The value for $G_P(H_2O_2)$ varied from 0.36 at pH 9.65 to 0.76 at pH 0.4. The yield $G_P(OH)$ was 2.84 in the pH range 6 to 9.65 but dropped to 2.40 at pH 0.4.

Several studies have shown effects of solutes on the yields of molecular H_2 and H_2O_2. Schwarz (71) found a lowering of the molecular H_2 yield by Cu^{++} and NO_2^- in the concentration range above 10^{-5} M. A similar lowering of the H_2 yield was reported by Ghormley & Hochanadel (86) for O_2, H_2O_2, and Ce^{+4}, by Hart (87) for Cu^{++}, by Allen & Rothschild (88) for Fe^{+3}. Sworski (89) showed that Cl^- lowers the molecular peroxide yield in a manner similar to that for Br^- (69). The effect was greater in 0.8 N acid than at pH 2, in line with the known pH dependence of the Cl^-+OH reaction. Cottin & Lefort (90) measured a yield of 1.6 for hydrogen production by Po^{210} α-particles in solutions containing either hydrazine, acetic acid, KBr, or acrylonitrile. Irradiating with gamma rays, the hydrogen yield was 0.5 in KBr solution and 0.34 in acrylonitrile solution. They point out that the "molecular" peroxide yield is more easily affected by solutes than is the hydrogen yield. A lowering of the molecular peroxide yield was reported by Collinson, Dainton & McNaughton (91) for acrylamide.

Additional studies of ferrous-ferric solutions have shown that the effects of oxygen, hydrogen and pH can be satisfactorily explained. In oxygen-free solutions, the competition of Fe^{+3} and Fe^{+2} for the H atom is important. Allen & Rothschild (88) found a ratio $Fe^{+3}+H/Fe^{+2}+H+H^+=7$ at pH 2 and showed the ratio to increase with pH. In the absence of H_2 and with sufficient Fe^{+3} to react with all H atoms, Fe^{+2} is oxidized with a yield equivalent to $2G_P(H_2)$. Added H_2 competes with Fe^{+2} for OH radicals thereby lowering the yield for oxidation. The ratio $H_2+OH/Fe^{+2}+OH=0.2$ at pH 2 and increases with pH. Allen & Hogan (7) showed that in the presence of oxygen the principal competition is that of Fe^{+3} and Fe^{+2} for the HO_2 radical. The reaction with Fe^{+3} is favored at higher pH, possibly as a result of HO_2 ionization (92). The minimum yield for Fe^{+2} oxidation is again equivalent to $2G_P(H_2)$. Ghormley & Hochanadel (93) showed that in oxygen saturated 0.8 N H_2SO_4, at sufficiently high concentrations, Fe^{+2} can compete with O_2 for H atoms and thereby lower the yield for Fe^{+2} oxidation.

Hart (87) studied the effect of added cupric ion on the oxidation of ferrous sulfate both in the presence and absence of oxygen. The net reaction in both cases under the proper conditions of concentrations and pH, is the formation of "molecular" hydrogen and the oxidation of an equivalent amount of ferrous ion. Hart (94) also studied the radiolysis of formic acid-ferric sulfate solutions in the pH range from 0.3 to 2.5. The principal products were H_2, CO_2, and Fe^{++}, and the main features of the proposed mechanism are reactions of formic acid with either H or OH giving the formate radical which reduces ferric ion. Ferric ion also competes for H atoms. At pH 2, the yield of ferrous ion was 6.33. This should be equal to $G_P(H)+G_P(OH)$.

Vermeil (95) studied the effects of many different hydrocarbons on the oxidation of ferrous sulfate by α particles, x-rays, and γ-rays, both in the presence and absence of oxygen. In the absence of oxygen either enhancement or inhibition was observed depending on conditions of intensity, total dose, and concentration. In the presence of oxygen, oxidation always occurred.

In the radiolysis of ceric sulfate solutions, Ce^{+4} is reduced by H (or HO_2) and H_2O_2 and the Ce^{+3} is oxidized back to Ce^{+4} by OH (76). The net yield is equal to $2G_P(H_2O_2)+G_P(H)-G_P(OH)$. Challenger & Masters (96), using labelled Ce^{+3} showed oxidation of Ce^{+3} by OH radicals as postulated by Allen (76). In nitric acid solution the yield for ceric reduction was enhanced to 8.3 while that for Ce^{+3} oxidation was reduced to 1.7. They also studied the radiation induced exchange of Tl^{+1} and Tl^{+3} and found a chain reaction involving Tl^{+2}. Sworski (97) showed that Tl^{+} ion enhances the yield for ceric reduction from 2.52 to 7.85. The added Tl^{+} reacts with OH to form Tl^{+2}thus preventing the back reaction $Ce^{+3}+OH$. The Tl^{+2} then reduces ceric ion. The yield for ceric reduction in the presence of Tl^{+} is equivalent to $2G_P(H_2O_2)+G_P(H)+G_P(OH)$ and the yield for Tl^{+3} formation is equivalent to $G_P(OH)$. Sodium nitrate increased the yield for ceric reduction by the same amount both in the presence and absence of Tl^{+}. The effect was attributed to "direct action" on the NO_3^-, possibly by transfer of energy from excited water molecules or by sub-excitation electrons.

Spencer & Rollefson (98) irradiated ceric sulfate with 50 kv x-rays in the presence of formic acid, the principal products being Ce^{+3}, CO_2, H_2, and O_2. This reaction is similar to the ferric ion—formic acid reaction except for the action of H_2O_2. The overall stoichiometry can be explained by reaction of HCOOH with OH to give HCOO, and reduction of Ce^{+4} by H or HO_2, HCOO, and H_2O_2. Under suitable conditions the yields of the various products should be: $G(Ce^{+3})=G_P(H)+G_P(OH)+2G_P(H_2O_2)$; $G(O_2)=G_P(H_2O_2)$; $G(CO_2)=G_P(OH)$.

In the gamma radiolysis of nitrite solutions, Schwarz & Allen (99) showed hydrogen and hydrogen peroxide were initial products, and nitrate was produced only after sufficient peroxide had accumulated. The principle feature of the mechanism is reaction of NO_2^- with H and OH to give NO and NO_2 which react with each other to give NO_2^- back. As H_2O_2 is formed it competes for H giving more OH and hence an excess of NO_2 which hydrolyzes to give NO_3^-. From the mechanism, the H atom yield was estimated to be 2.4.

Collinson, Dainton & McNaughton (91), using acrylamide to scavenge H and OH radicals (which induced polymerization), measured a maximum molecular peroxide yield of 0.8 in neutral solution. By adding ferric ion which terminated the polymerization chains, they were able to evaluate the yield for chain initiations, and from that the sum $G_P(H)+G_P(OH)$. The value obtained at pH 1.13 was 6.1.

In aqueous hydrazine solutions Dewhurst & Burton (100) found the

principal products to be ammonia, nitrogen, and hydrogen. Ammonia was produced at the same rate as hydrazine disappeared, with a yield of 5.2. Nitrogen and hydrogen were formed with half this yield. From the proposed mechanism in which the free radicals H and OH both react with hydrazine, the yield of ammonia is equal to the sum $G_P(H)+G_P(OH)=5.0$ to 5.2.

Wilkinson & Williams (101) described some interesting work on the irradiation of phosphate esters of the monoalcohols with 1 Mev electrons and Co^{60} gamma rays. In the presence of oxygen at pH 8, inorganic phosphate, acyl phosphate, hydrogen peroxide, and aldehyde were formed. The observed yields were explained by reactions with free radicals produced in the decomposition of the water. The derived values of 3.2 H, 3.2 OH and 0.5 H_2O_2 are in fair agreement with values listed in Table III.

Baxendale & Smithies (102) used 190 kv x-rays to irradiate aqueous benzene solutions with and without ferric ion or cupric ion present. On the basis of the proposed mechanism they were able to evaluate the yields of the intermediates produced in 0.1 N H_2SO_4 giving: $G_P(OH)=2.4$, $G_P(H)=3.1$, $G_P(H_2O_2)=0.57$, and $G_P(H_2)=0.22$.

In the gamma radiolysis of aqueous methanol solutions, McDonnell (103) found that formaldehyde is formed by a "direct action" mechanism, while ethylene glycol is formed predominantly via reactions with free radicals produced by water decomposition. According to Henley & Schwarz (104) acetaldehyde, acetic acid, and ethanol were principal products produced in the radiolysis of water containing dissolved ethylene and oxygen.

Maxwell *et al.* (105 to 108) published a series of papers on the decomposition of aqueous solutions of the amino acids glycine and alanine by 50 Kv x-rays and electrons. Principal products in the decomposition of glycine were NH_3, HCO-COOH, H_2, CH_3COOH, CO_2, HCHO, CH_2NH_3, HCOOH, with yields ranging from 4 to 0.2 in the order given. The decomposition of alanine paralleled that of glycine.

From the dependence of yields on concentration of acetic acid in water, Garrison *et al.* (109) concluded that, of the products of radiolysis with deuterons and helium ions, CO_2, CH_4, C_2H_6, and CO_2, were formed primarily by "direct" action, while succinic acid formation was by indirect action. H_2O_2 and part of the H_2 were "molecular" products of water decomposition. The use of I_2 and I^- scavengers aided in establishing mechanisms. Weeks & Garrison (110) made a similar study of aqueous glycine solutions. Haymond & Garrison (111) also studied the effect of oxygen in the radiolysis of acetic acid. The succinic acid yield is reduced, the CO_2 and H_2O_2 yields increased, and glycolic acid, glyoxylic acid, and formaldehyde are new products as a result of the formation of peroxy radicals.

Ballantine *et al.* (112) found a square root dependence on intensity in the gamma ray polymerization of 1-vinyl-pyrrolidinone. On irradiating vinyl polymers in aqueous solution, Charlesby & Alexander (113) observed that, in general, degradation occurs at concentrations <0.5 per cent, and cross linking and gelation occur at higher concentrations. Polymethylacrylic acid

was degraded at all concentrations. Results could be explained by the "end linking" process. Fox & Alexander (114) studied post-irradiation effects in the polymerization of methacrylic acid.

Several papers on radiation chemistry were presented at the Conference of the Academy of Sciences of the USSR on the Peaceful Uses of Atomic Energy in July 1955. Each of these papers was a review covering the work of a number of people on a number of different subjects. Bach (115) described studies of the radiolysis of aqueous solutions of iron salts, potassium iodide, and sodium nitrate using 90 kv x-rays. In addition to standard gas and solution analyses following irradiation, they measured changes during irradiation using polarographic measurements and measurements of redox potentials. These methods have been little used by others, and warrant further development. They observed that at concentrations >0.1 M a "direct" action on the solute occurs which they attribute to reaction of the solute with excited water molecules. Proskurnin, Orekhov & Barelko (116) described the radiolysis of a large variety of systems including aqueous solutions of Fe^{++}, NO_3^-, benzene, and alcohols, and also anhydrous alcohols and solid KNO_3. The yields of $\sim$60 observed for ferrous oxidation in 0.01 M ferrous solutions in 4N sulfuric, hydrochloric or phosphoric acid, are probably incorrect (117). On heating irradiated potassium nitrate crystals above 129°C., a back reaction occurred, indicating the existence of NO_3, NO_2, and O in the irradiated crystals. Veselovsky (118) reported studies of a variety of radiolytic reactions in aqueous solution. In degassed acid solution under gamma irradiation, a platinum electrode attained a stable potential close to that of the hydrogen electrode. This was cited as evidence for H atom formation. With oxygen present a potential 1 volt greater was attributed to the formation of HO_2. ZnO enhanced H_2O_2 formation in oxygen-saturated water attributable to electron transfer reactions at the surface of the particles. Dolin & Ershler (119) studied the radiolysis of water in the presence of H_2 and O_2, using radiations from a heavy water reactor, fission recoil particles, and Co^{60} gamma radiation. Both the decomposition reaction and the back reaction were studied. In many respects the results and interpretation are similar to those reported previously (120). They observed an effect of oxygen on the steady state hydrogen pressure which may be attributed to an effect of oxygen on the molecular hydrogen yield.

Hochanadel, Ghormley & Sworski (121) found that in concentrations above 60 per cent, sulfuric acid is decomposed by gamma rays, and SO_2 is produced. The presence of O_2 or H_2O_2 suppressed SO_2 formation. Failure to observe SO_2 formation in more dilute solutions may result from a rapid back reaction. Boyle *et al.* (122) made a thorough study of the decomposition of water by fission recoil particles. The H_2 yield depended markedly on U^{235} enrichment (type of radiation) and on the uranium concentration. The hydrogen yield increased with decreasing uranium concentration giving an extrapolated value of 1.8 at zero concentration, the same as that for alpha particles. Dawson & Hall (123) and Yakovlev & Kosyakov (124) reported americyl ion is reduced by its own alpha radiation.

Markham (125) reviewed the photo-catalytic properties of oxides, a subject closely related to the radiolysis of solutions. It appears that electron transfer reactions at the surface of the particle yield the free radical intermediates H and OH which can produce oxidation or reduction of added solutes such as $O_2 \rightarrow H_2O_2$. Grossweiner (126) presented such a mechanism for the photochemical production of hydrogen peroxide catalyzed by mercuric sulfide. Griffing (127) reviewed the possible mechanisms for chemical effects produced by ultrasonics. A hypothesis based on high local temperatures caused by the adiabatic compression of small gas bubbles was suggested.

Solids

The paramagnetic resonance absorption method has been used by a number of workers to study the trapping and subsequent reactions of species containing unpaired electrons (e.g. free radicals). The most successful application of this method has been the positive identification by Livingston, Zeldes & Taylor (128) of the H atom in frozen acid solutions irradiated with gamma rays. Matheson & Smaller (129) have observed paramagnetic species in gamma-irradiated ice at 77°K, which they attribute to H and OH. These disappear on warming to 115°K. Solid ammonia and solid formic acid were studied also. Bamford *et al.* (130), Bijl & Rose-Inness (131), and Wall and Brown (see 20) studied the trapping of free radicals in polymers.

Wolfgang, Rowland & Turton (132) described the labelling of glucose in nonlabile positions by the simple method of irradiating a Li_2CO_3-glucose mixture with thermal neutrons to produce recoil tritons by the $Li^6(n, \alpha)H^3$ reaction. A surprisingly large fraction of the recoil tritons end up in the glucose. The mechanism involved offers a challenge to the radiation chemists as well as the hot atom chemists. Sharman & McCallum (133) studied chemical effects in the reactions $Cl^{35}(n, \gamma)Cl^{36}$ in sodium chlorate and $C^{12}(\gamma, n)C^{11}$ in sodium carbonate. Yankwich & Corman (134) analyzed the radio carbon compounds produced on dissolving in water, neutron-irradiated ammonium sulfate crystals. Burns & Williams (135) studied the chemical effects of color centers in additively colored and x-ray-irradiated alkali halide crystals. On dissolving in water, free halogen was found, and also the polymerization of acrylonitrile was initiated.

Pringsheim (136) measured the absorption spectrum of $NaNO_3$ exposed to x-rays and found absorption bands attributable to NO_2^- and to color centers. Following irradiation at -190°C., the color center band was bleached by heat or ultraviolet, but the NO_2^- band was not.

Rosenwasser, *et al.* (137) found that yields for decomposition of explosives were comparable to those for stable materials.

In a review article, Charlesby (138) discussed degradation, cross linking, gel formation, and protection in the irradiation of various types of polymers. He also studied cellulose (139), silicones (140), rubber (141), long chain olefins and acetylenes (142), "end linking" (143), and protection (144).

Karpov (145) and others studied the effects of gamma rays and fast electrons on high polymers, mainly vinyl polymers. Changes studied were

degradation and cross linking, as indicated by measurements of mechanical properties, change in structure of polymeric crystals by x-ray diffraction, and changes in molecular structure by infra red analysis. It was suggested that transfer of energy within the molecule results in preferential breaking of weak bonds. In the presence of air, oxidation reactions occurred. The changes were related to molecular structure and mechanisms were proposed. From studies of the reticulation of polyethylene by x-rays, Chapiro (146) calculated a primary radical yield of 5.1. Chapiro & Migirdicyan (147) studied the polymerization of methyl methacrylate.

In a symposium on the Effects of Radiation on Polymers (20) Burton & Reddy presented a general discussion of mechanisms; Schultz & Bovey presented yields for crosslinking and main chain fission in the polyacrylates and polymethacrylates; Miller, Lawton & Balwit discussed the effects of molecular structure on cross-linking, degradation, and production of various types of unsaturation in hydrocarbon polymers; Warrick measured a yield of three cross linkages per 100 ev in di-methlylpoly-siloxane. Phenyl substitution increased the resistance to radiation. Bopp & Sisman (20, 148) and also Cole discussed changes in physical properties of plastics. Schulz (22) applied statistical theory to explain random cross linking and degradation of polymers. Yen-Hsuing Feng & Kennedy (149), Stark & Garton (150), and Fowler & Farmer (151), measured changes in electrical properties on irradiation of plastics. A bibliography on radiation effects in high polymers was assembled by Pecjak & Sun (22), and on food sterilization by radiation by the Quartermaster Food and Container Ins., Chicago, NP-5543 (1955).

Organic Liquids

Bouby & Chapiro (152) and Medvedev (153) used DPPH as scavenger, Weber, Forsyth & Schuler (154) used I_2, and Seitzer & Tobolsky (155) used initiation of polymerization to evaluate radical yields in the radiolysis of organic liquids. There is a need for further development of scavenger and tracer methods to identify radical intermediates, to measure their yields, and to determine the position in the substrate molecule from which the radical originated. In general the yields range from 1 to 25–50 in the order: aromatics <aliphatics <oxygenated compounds <halogenated hydrocarbons.

Polymerization kinetics were studied by Chapiro *et al.* (156), Bouby *et al.* (157), and by Medvedev (153). Energy transfer was studied by Burton, Berry & Patrick (158), Furst & Kallman (159), and Krenz (160) by means of fluorescence measurements, and by chemical measurements (161), Bakh (162) observed the formation of three types of peroxides, R_1OOR_2, ROOH, and H_2O_2, in the radiolytic oxidation of various organic compounds. Harmer, Martin & Anderson (163) described the chain chlorination of aromatic hydrocarbons by gamma rays.

McDonnell & Gordon (164) showed, in comparing the decomposition of methanol by gamma rays and 28 Mev helium ions, that formation of formaldehyde is favored for the heavy particle radiation and ethylene glycol by the lighter particles. Allen & Schuler (165) had found no difference in hydro-

gen yield from cyclohexane on varying the energy of He^+ ions or deuterons. Sworski & Burton (166) had found an effect of particle velocity in the radiolysis of aromatic hydrocarbons. It is reasonable to expect the formation of higher excited states to be favored on passage of slower particles. Also, those products which are formed by radical combination rather than by reaction of radicals with substrate molecules, would be favored in heavy particle radiation where radicals are produced close together in the tracks.

On materials more directly related to Radiobiology it is only possible to mention some of the studies carried out. Barron (167) summarized some of the chemical effects of radiations on materials of biochemical importance. Kuzin (168) has also discussed the biochemical actions of radiations. There have been studies by Barron, Ambrose & Johnson (169) on amino acids and proteins; by Khenokh & Lapinskaya (170) on amino acids; by Shapiro & Eldjarn (171) on cysteamine and cystamine; by Dale & Russell (172) on cystein, cystine, and glutathione; by Bonet-Maury & Patti (173) on catalase; by Lemmon, Parsons & Chin (174) on choline chloride and its analogs; by Little & Kent (175), Koyenuma (176), Cox *et al.* (177), and Daniels, Scholes & Weiss (178) on nucleic acids; by Stein (179) and by Laser (180) on cytochrome C reduction; by Patti (181) on uranine S and sodium eosinate; by Allinson *et al.* (182) on cortisone and deoxycorticosterone.

Dosimetry

The chemical dosimeter in widest use at present and the one which still offers the most advantages is the oxidation of ferrous sulfate in air saturated 0.8 *N* sulfuric acid. Schuler & Allen (183) determined the extremely accurate yield of 15.45 ± 0.11 using 2 Mev electrons from a Van de Graaff generator. Donaldson & Miller (184) obtained the value 15.4 ± 0.8 using $P^{32}\beta^-$ particles. These results are in agreement with previously determined calorimetric values (185, 186). Values reported by Hochanadel & Ghormley (185), and by Weiss & Bernstein (187), based on ionization chamber measurements are in agreement with the value 15.6 provided the value 33.6 to 34 is used for W (energy per ion pair for air) and 1.03 to 1.04 for $S_{poly.}/S_{air}$ (the ratio of stopping power per electron of the polystyrene ionization chamber relative to that for air) are used. As shown by Dyne (188), some of the high values of $\sim$20 were caused by faulty geometry in ion chamber measurements. By making additional corrections Farmer, Rigg & Weiss (189) have brought their previously reported value down to 15.6. There is now general agreement on this value for x-rays, γ-rays, and electrons over the energy range from about several tenths to several Mev.

Schuler & Allen (165) using deuterons and alpha particles produced by a cyclotron, found yields for ferrous oxidation ranging from 6 for 5 Mev alpha particles to 9 for 35 Mev alpha particles, and from 10 for 6 Mev deuterons to 11.6 for 19 Mev deuterons. A plot of yields for the two types of particles showed a continuous decrease in yield with increasing rate of energy loss along the particle track. Hart & Gordon (190) extended the measurements to higher energy densities using Po^{210} alpha particles and mica ab-

sorbers and found the ferric yield to drop from 6.2 for 5.3 Mev alphas to 2.1 for 0.7 Mev alphas. Ehrenberg & Saeland (191) had also measured the ferric yield for various radiations including uranium fission fragments which gave a yield 3.0.

Bernstein & Schuler (192) measured the scattered radiation inside a cylindrical Co^{60} γ-ray source. In a thick source, considerable scattering occurs in the source itself giving an appreciable flux in the 0.25 Mev region. In the radiolysis of materials containing heavy atoms, considerable care should be exercised in measuring the dose received.

Spencer & Attix (193) and Burch (194) presented new theories of the cavity ionization chamber which take into account the effects of electrons in the delta ray tracks. Goldwasser *et al.* (195) studied the effect of polarization on the energy loss of 15.7 Mev electrons in the polymers teflon and Kel-F plastic. The losses agreed with theory and were about $4\frac{1}{2}$ per cent lower in teflon and $15\frac{1}{2}$ per cent lower in Kel-F plastic than in the equivalent gas. Ellis, Rossi & Failla (196) found the stopping powers of water vapor and liquid water to be the same (± 5 per cent) for Po^{210} alpha particles. Ellis (197) had previously shown that polystyrene and acetylene also have the same atomic stopping power for low energy alpha particles. Aniansson (198) measured the range of Po^{210} particles in water at 25°C. and in several organic liquids. In water, the range of 39.9 μ was 2.7 per cent longer than that computed by the Bragg law. A similar discrepancy was noted for five other liquids. Johns *et al.* (199), using a sensitive thermistor, measured the Co^{60} gamma heating in C and Al. By comparison with ionization in C and Al walled chambers they arrived at the value 33.2 for W in air. Gray reported (200) that measurements of Emery gave a value 33.9 for W in air for x- and γ-rays in agreement with that of Weiss & Bernstein (187). See the section on gases for other measurements of W. By means of scintillation spectrometry, Bruce & Johns (201) measured the electron spectrum at various positions in a water phantom irradiated with a collimated beam of Co^{60} γ-rays.

Radiation sources and industrial applications.—Burton, Ghormley & Hochanadel (202), Charlesby & Flint (203), Eastwood (204), and Rabin & Price (205) described cobalt sources. The energy available in the various fission products, and possible beneficial uses for which this energy can be utilized were discussed by Glueckauf (206), Wright (207), and Young & Allen (208). Martin (209) surveyed the use of ionizing radiations to promote chemical reactions, Brownell *et al.* (210) discussed the pasteurization of meats, and Clifcorn (211) discussed the sterilization of foods and drugs.

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QUANTUM THEORY

By W. Moffitt and C. J. Ballhausen[1]

Department of Chemistry, Harvard University, Cambridge, Massachusetts

Previous reviews with the same or similar advertisement have concerned themselves with the theory of the electronic structure of molecules. No mention has been made, however, of perhaps its most strikingly successful variant, namely the crystal field theory. It seems unnecessary, therefore, to offer excuses for any lack of balance imposed on the series if we confine ourselves to transition-metal complexes in the present issue.

The crystal field theory has a long history. It was first developed by Becquerel (13), Bethe (15, 16), Kramers (62, 63, 64) and Van Vleck (97, 98). By 1932, with the work also of Gorter (37), Penney and Schlapp (82, 86), its most important features were already recognized and had explained many of the magnetic properties of salts of the transition metals and of the rare earths.[2] Essentially the same theory is used to-day in order to describe a much wider variety of effects, ranging from trends in the heats of hydration and the colours of aqueous ions to the hyperfine structure of their paramagnetic resonance spectra. Indeed, the only nontrivial many-electron systems which are more completely understood are free atoms and ions.

Our aim has been to provide both a review and a bibliography of the theory, but we separate these goals in our treatment. In a chapter of this size, it is impossible to develop the whole theory, so we have tried to cover those aspects of it which are of most concern to chemists. Where to be general is to risk being obscure, we have chosen simple examples to illustrate the argument; it should be stressed that these are chosen for no other reason. In the same way, the experimental values quoted are not to be regarded as in any way representative of an enormous number of publications which we have not attempted to compile. We have not tried to serve history, nor have we been at pains to accord priorities: many of the ideas that have proved to be most fruitful have been propounded in the course of interpreting particular experiments; it would be a major undertaking in a form of scholarship with which we have little familiarity to find their true originators. Finally, we are chemists writing for chemists. Our emphasis and notation have therefore differed at times from those of the physicists primarily responsible for the theory. Our survey of the pertinent literature was completed in December, 1955.

Crystal Field Theory

The crystal field theory concerns itself with the behaviour of rare earth

[1] On leave of absence from Chemical Laboratory A, Technical University of Denmark, Copenhagen.

[2] At the same time, Pauling (80) was developing a superficially very different approach which has become a standard part of chemical thinking and symbolism (vide infra).

and transition-metal salts, their solutions and complexes. It treats the metal ions as if they were subjected to electrostatic fields of force arising from the groups by which they are surrounded. Thus the anions, the waters of crystallization or of solvation, and the other ligands with which they are most intimately associated are assigned rather passive roles. These may, to be sure, be polarized by the presence of the cation they stabilize, but the motions of their electrons are assumed to remain unaffected by such factors as the optical excitation of the cation: the ligands are supposed to provide a potential field for the central ion which is the same for its ground as for its lower excited states.

The quantal treatment for this model is therefore easily formulated. The Hamiltonian for the cation consists of two terms:

$$\mathcal{H} = \mathcal{H}_F + \mathcal{V},$$

where $\mathcal{H}_F$ is the Hamiltonian for the free ion and $\mathcal{V}$ is the potential provided by its ligands. It is supposed that the eigenfunctions and eigenvalues of $\mathcal{H}_F$ are known. Accordingly, the potential $\mathcal{V}$ is regarded as a perturbation which determines the electronic motions and term values of the cation in the crystal, solution or complex.

Since the unperturbed functions are solutions of problems with full spherical symmetry, it is convenient to expand $\mathcal{V}$ in a series of normalized harmonics:

$$\mathcal{V} = \sum_i \sum_n \sum_m \mathcal{Y}_{nm}(\theta_i, \phi_i)\mathcal{R}_n(r_i),$$

the first summation being over the several electrons of the cation.[3] By far the most important term in this development is the spherically symmetric term with $n=0$:

$$\mathcal{V}_R = \sum_i (4\pi)^{-1/2}\mathcal{R}_0(r_i).$$

Thus $\mathcal{V}_R$ is responsible for the greater part of the lattice energy or heat of solution of a given cation. On the other hand, it has little effect on the optical and magnetic properties of crystals since, to a first approximation, it will only give rise to a uniform shift of all levels with the same number of d or of f electrons.[4] Of the remaining terms in the expansion, many may be

[3] The ligands are sometimes replaced by supposedly equivalent point charges, dipoles and so forth, in which case $\mathcal{R}_n(r_i)$ takes the form $a_n r_i^n + b_n r_i^{-(n+1)}$. On the other hand, if $\mathcal{V}$ is more nearly a self-consistent field, say, it will no longer satisfy Laplace's equation and $\mathcal{R}_n$ is a more general function of r_i. In most applications, the specific form of $\mathcal{R}_n$ is in any case of little importance, parameters containing it being determined semi-empirically.

[4] If it is supposed that the radius of the free cation is the same in its ground and lower excited states—that is, for example, that the radial parts of the d orbitals are the same both for the ^4F and ^4P levels of Cr^{+++}—, then the influence of $\mathcal{V}_R$ will only be felt as the result of second-order interactions with highly excited configurations in which, say, a $3d$ electron is promoted to a $4d$ level.

neglected. For example, if the effects to be described arise from degeneracies in incompleted d or f shells, all harmonics of odd order are ineffective; again, when only d electrons are involved, all potentials after the fourth-order terms exert no influence.[5] And finally, the potential $\mathcal{V}$ must have the same symmetry as the cationic site: if this is octahedral, $\mathcal{V}$ must remain invariant under all operations of O_h. It should be remarked that to good approximation $\mathcal{V}_R$ is the only component of $\mathcal{V}$ that is operative on S states in general—and therefore on closed shells and half-filled shells of maximum multiplicity in particular. Rather crudely, one may regard $\mathcal{V}_R$ as providing a spherical hole of constant potential, outside which it offers an infinite potential barrier to the cationic electrons; this view has the merit that it emphasizes the dependence of $\mathcal{V}_R$ on the effective ionic radius.

Octahedral Fields

Many of the principal features of the transition-metal ions emerge from the following simple model. The ions, whose lower electronic states all arise from the configurations (argon) $(3d)^n$, are situated in fields of perfect octahedral symmetry. Since the representation of O_h spanned by the harmonics of order less than five contains the identical representation only twice ($n=0$, 4), it follows that

$$\mathcal{V} = \mathcal{V}_R + \mathcal{V}_O,$$

$$\mathcal{V}_O = \sum_i \left\{ Y_{40}(\theta_i, \phi_i) + \sqrt{\frac{5}{14}} \left[Y_{44}(\theta_i, \phi_i) + Y_{4,-4}(\theta_i, \phi_i) \right] \mathcal{R}_4(r_i) \right\}.$$

The polar axis here, as elsewhere, is chosen to coincide with a particular fourfold axis of the octahedron; also, the Y_{nm} are normalized spherical harmonics whose phases are prescribed by Condon & Shortley (28). The crystalline forces are supposed to be much stronger than those attributable to spin-orbit coupling in the free ions. As has been remarked, $\mathcal{V}_R$ is very large and corresponds to the replacement of six ligands by a spherically symmetric field. Thus, if $\mathcal{V}$ represents six waters of crystallization, then we should expect the variation resulting from $\mathcal{V}_R$ in absolute term values to behave monotonically on going from Ti^{+++} to Co^{+++}, or from Ti^{++} to Zn^{++}, reflecting a more or less continuous decrease in the radii of the free ions. The potential $\mathcal{V}_O$, on the other hand, is more specific stereochemically, and acknowledges the existence of six negative groups at the respective vertices of the octahedron. It will remove the orbital degeneracy of the d electrons, since these will prefer to avoid regions where the electronic density of the ligands is greatest. However, the extent to which the orbital alignments are determined by $\mathcal{V}_O$ will depend on the number of electrons present and their correlative interactions with one another. Accordingly the influence of $\mathcal{V}_O$ on the ionic

[5] Any matrix representation of an odd order potential in a basis of orbitals with the same parity vanishes identically. Again, the direct product of two d orbital sets spans no representations of the rotation group of order higher than four.

term values will vary as a function of atomic number in a much more complicated manner than that of $\mathcal{V}_R$.

Single d electron.—The effect of the octahedral field is most clearly shown by considering the Ti^{+++} ion, which has a single $3d$ electron outside an argon shell. If higher configurations are ignored, $\mathcal{V}_O$ has no effect on the closed shell but simply splits the fivefold orbital degeneracy of the ion. The qualitative behaviour is easily determined by group theory, which shows that the reducible representation spanned by the five d orbitals contains the irreducible representations E_g and T_{2g} of the octahedral group O_h, the former being doubly degenerate and the latter threefold degenerate. The ^2D term therefore splits into ^2E_g and $^2T_{2g}$ levels.[6] More specifically, it is easily shown by symmetry that

$$t_{2g}^0 = \frac{1}{\sqrt{2}}(d\delta_+ - d\delta_-), \qquad t_{2g}^+ = d\pi_+, \qquad t_{2g}^- = d\pi_-;$$

$$e_g^a = d\sigma, \qquad e_g^b = \frac{1}{\sqrt{2}}(d\delta_+ + d\delta_-),$$

where $\sigma, \pi_\pm, \delta_\pm$ refer to $m_l = 0, \pm 1, \pm 2$ respectively. We see that the densities of the e_g electrons are directed towards the vertices of the octahedron, and therefore towards the ligands, whereas those of the t_{2g} electrons avoid these regions. Since the ligands are either anions or molecules, the negative ends of whose dipoles are directed towards the cation, it is evident that the t_{2g} orbitals are more stable than the e_g orbitals. Explicitly, their energies may be written

$$\epsilon(e_g) = \epsilon_0 + 6Dq, \qquad \epsilon(t_{2g}) = \epsilon_0 - 4Dq,$$

$$-4Dq = \int \phi^*(t_{2g}^0)\mathcal{V}_O\phi(t_{2g}^0)d\tau.$$

By convention, the overall splitting of a single d electron under $\mathcal{V}_O$ is set equal to $10Dq$, where $Dq > 0$ (86).[7]

The electronic spectrum of the $[Ti(H_2O)_6]^{+++}$ ion would be described as arising from the transition $(t_{2g})^{-1}(e_g)$, and be assigned an excitation energy of $10Dq$. If the symmetry is close to octahedral, we should expect a single weak band, since no change in parity occurs. Such a band is indeed found for the ion, with a maximum at 4900Å, corresponding to $Dq = 2040$ cm^{-1}. It is very broad, however, and shaded to the blue (39), suggesting that the degeneracies are partially resolved by fields of lower symmetry. Nevertheless, one might expect to understand, for example, the heat of hydration of the Ti^{+++} ion on the basis of $\mathcal{V}_R$ and an additional stabilization, $4Dq = 8160$ cm^{-1}, due to $\mathcal{V}_O$.

[6] When referring to the orbitals themselves, we call them e_g, t_{2g} respectively; the distinction is trivial for a single d electron in the same way that the terms of the hydrogen atom may be called ns, np, $\cdots$, or n^2S, n^2P, $\cdots$.

[7] The coefficients $+6$ and -4 may most easily be determined on noting that $\mathcal{V}_O$ makes no contribution to S states—such as that found on filling all d orbitals.

There is a well-known reciprocity in atomic spectroscopy between electrons and "holes." Thus the terms arising from $n(\leqq 5)$ electrons outside an argon shell are the same as those arising from $(10-n)$ electrons outside the same shell or, equivalently, of n holes in the completed d^{10} shell. Since the interaction between two holes is the same repulsive coulombic term as between two electrons, these terms are in the same order for both d^n and d^{10-n} configurations. However, since the magnetic moment due to the circulation of a positron is the opposite of that due to an electron, the multiplet structure is inverted. A similar reciprocity exists in crystal field theory, say, between Ti^{+++} and Cu^{++}, whose configuration is d^9. It is clear that the ^2D state of Cu^{++} also splits into ^2E_g and $^2T_{2g}$ terms. But the order of these levels is now inverted because the electrostatic field due to the ligands has an opposite effect on holes as on electrons.

In order to explain the spectrum of the Cu^{++} aquo complex, a very broad and weak system with a maximum around 8000Å, it is necessary to invoke a considerable contribution from fields of lower symmetry: the hydrated ion is a distorted octahedron (17).

Weak fields.—In dealing with more than one electron or one hole, it is convenient to distinguish between two limiting cases. In both, the splitting due to the octahedral field is much larger than that due to spin-orbit coupling. But in the one case, which we pursue now, the crystal field is small with respect to the separation of different groups of multiplets, such as the ^4F and ^4P levels of Cr^{+++}. And in the other, it is large with respect to these intervals. They are, respectively, the weak and strong field limits. The most general, that is, the intermediate case is also the most common and will be considered later. As a rough, but by no means rigorous criterion, it is found that Pauling's "ionic" complexes correspond to weak fields and his "covalent" complexes to strong fields (81).

TABLE I

STATES AND ENERGIES IN WEAK OCTAHEDRAL FIELDS

Ground State of Free Ion	Octahedral States and Energies (Dq units)
d:^2D	$^2T_{2g}(-4)$, $^2E_g(+6)$
d^2:^3F	$^3T_{1g}(-6)$, $^3T_{2g}(+2)$, $^3A_{2g}(+12)$
d^3:^4F	$^4A_{2g}(-12)$, $^4T_{2g}(-2)$, $^4T_{1g}(+6)$
d^4:^5D	$^5E_g(-6)$, $^5T_{2g}(+4)$
d^5:^6S	$^6A_{1g}(0)$
d^6:^5D	$^5T_{2g}(-4)$, $^5E_g(+6)$
d^7:^4F	$^4T_{1g}(-6)$, $^4T_{2g}(+2)$, $^4A_{2g}(+12)$
d^8:^3F	$^3A_{2g}(-12)$, $^3T_{2g}(-2)$, $^3T_{1g}(+6)$
d^9:^2D	$^2E_g(-6)$, $^2T_{2g}(+4)$

$A_{1g}=\Gamma_1$; $A_{2g}=\Gamma_2$; $E_g=\Gamma_3$; $T_{1g}=\Gamma_4$; $T_{2g}=\Gamma_5$

In the case of weak fields, therefore, the quantum numbers L, S of the central ion retain their validity, and we have only to determine how a given L, S level is split by the octahedral field $\mathcal{V}_O$, without considering the possibility that different levels may interact under it. To a first approximation, the ground states of the aquo complexes of the ions in the first transition period may be treated in this way. The qualitative features are again most simply obtained by group theory. The symmetries of the states into which the ground level of the free ion splits are listed in Table I, at the bottom of which Bethe's notation for representations of the octahedral group is also given, to facilitate comparisons (15). These states are listed in increasing order of excitation. Thus the ground state of the Cr^{+++} ion in the field is the orbitally nondegenerate ${}^4A_{2g}$ state. Following such term symbols, numbers are given parenthetically which assess their energies due to $\mathcal{V}_O$ in terms of the parameter Dq for a single electron: the Cr^{+++} ion, for example, is stabilized by some $12Dq$ in the limit of weak fields.[8]

It is interesting to find how many electrons, on the average, occupy the t_{2g} and how many the e_g orbitals in the ground states of the crystalline ions. In general, these numbers will not be integers since, in weak fields, the tendency for maximum field stabilization—namely, the preferential filling of the t_{2g} shell—is subordinate to the forces of correlation between the electronic motions. The expectation values for these occupation numbers are most simply determined from Table I, by inspection: in order that the two electrons

[8] There are many different ways of obtaining these energies. The most general and also perhaps the most simple method for the weak field case is to observe that—within a manifold spanned by the $(2L+1)$ orbital states of given L, S, M_S—the matrix representation of $\mathcal{V}_O$ is directly proportional to that of the operator.

$$L_x^4 + L_y^4 + L_z^4 - \frac{1}{5} L(L+1)[3L(L+1) - 1]$$

$$= \frac{1}{20}[35\, L_z^4 - 30L(L+1)L_z^2 + 25L_z^2 - 6L(L+1) + 3L^2(L+1)^2]$$

$$+ \frac{1}{8}[(L_x + iL_y)^4 + (L_x - iL_y)^4].$$

(There appears to be a misprint in the table of operator equivalents given by Bleaney & Stevens (22), where the factor $\frac{1}{8}$ preceding the last expression is given as $\frac{1}{4}$.) It is obtained on replacing x_i, y_i, z_i by L_x, L_y, L_z in the symmetric, homogeneous form of writing the angular dependence of a typical term of $\mathcal{V}_O$: $(x_i^4+y_i^4+z_i^4-\frac{3}{5}r_i^4)$, taking account of the fact that whereas x_i, y_i commute, L_x, L_y do not. This, and analogous results for different coupling schemes and different potentials, may be proved using Wigner coefficients (91) or the results of section 9^2 in Condon & Shortley (28). The proportionality constant is now determined by evaluating a single element, chosen for its simplicity, in both matrices. For example, the eigenfunction for the $L_z=3$, $S_z=3/2$ component of d^3, ${}^4F$ may be written $|d\sigma d\pi_+ d\delta_+|$, where $|\cdots|$ denotes a normalized and antisymmetrized product, and the absence of bars over the orbital symbols means that these are to be taken with α spin. The diagonal element for this row in the matrix $\mathcal{V}_O$ is just $+3Dq$, and the corresponding element in its operator equivalent is $+9$.

of $^3F(T_{1g})$ should distribute themselves between these two levels and have energy $-6Dq$ under $\mathfrak{V}_O$, it is clear that on the average 9/5 must be found in the stable t_{2g} shell and only $\frac{1}{5}$ in the unstable e_g shell. For three, four, · · ·, eight electrons, these pairs of occupation numbers are (3, 0), (3, 1), (3, 2), (4, 2), (24/5, 11/5), (6, 2) respectively. In the excited states, of course, electron density is transferred from the t_{2g} to the e_g levels. Indeed, such numbers are entirely equivalent to prescriptions of energies.

[The general theory is described by Bethe (15), Van Vleck (98), Schlapp & Penney (86), Jordahl (52). Techniques are given by Wigner (108), Kramers (65), Condon & Shortley (28), Von der Lage & Bethe (107), Hellwege (43, 44), Stevens (91), Bell (14) and Judd (57).]

Applications of weak field theory.—The earliest applications of crystal field theory, in its weak field limit, were to the magnetic properties of salts. These are discussed later. At present we consider topics of greater chemical interest.

The lower electronic transitions may tentatively be assigned to excitations from the ground crystalline component to the higher ones. Thus the 5800Å system of the $[V(H_2O)_6]^{+++}$ ion (40) would be ascribed to the process $^3T_{1g} \rightarrow {}^3T_{2g}$. And similarly for the other ions. (In general, however, it is better to use intermediate field theory for such assignments.) These identifications enable one to determine the appropriate Dq in each case; for the V^{+++} aquo complex (d^2), we have $8\ Dq \approx 17{,}200\ cm^{-1}$.

Values of Dq, determined in this manner, have been used in order to rationalize the behaviour of the heats of hydration of the divalent and trivalent ions of the iron group. On the basis of the spherically symmetric potential $\mathfrak{V}_R$ alone, one would expect these heats to increase steadily on going from left to right across the periodic table—for the radii of the free ions, before solvation, decrease uniformly in this order. However, from this standpoint, the values for $Mn^{++}(^6S)$ and also for $Fe^{+++}(^6S)$ are anomalously low. This is no longer surprising when the additional stabilization conferred on the aquo complexes by the octahedral component $\mathfrak{V}_O$ of the field is taken into account. As an inspection of Table I will show, it is only the d^5 and d^{10} ions which do not benefit from this. On calculating the energies of stabilization from spectral data, the irregularities in the observed heats are almost quantitatively removed [Orgel (73)].

A related explanation has been given for the behaviour of the effective crystal radii of these ions. Empirically, it seems clear that these do not decrease monotonically as a function of atomic number, but show maxima at configurations d^4, d^5 and possibly again at d^9, d^{10}. Now it is clear that, for a given number of electrons, the more that are in the t_{2g} levels, the more closely may the ligands approach and, therefore, the smaller the crystal radius of the ion; occupation of the unstable e_g orbitals will imply a localization of electron density in the region of the approaching ligands which are accordingly repelled. The lowest crystal levels of the d^3, d^4 and d^5 configurations correspond successively to the occupation of the e_g orbitals by 0, 1 and 2 elec-

trons, and a ready explanation for the crystal radii is obtained [Santen & Wieringen (84)].[9]

In general, the longer wave-length bands, and in particular those which are attributed to transitions between states arising from the same free ion level, are very broad. The factors contributing to these widths may be described at this point, though they will often be applied in contexts where neither the weak field approximation, nor the assumption of perfect octahedral symmetry, are valid. The appropriate generalization of the argument is not difficult and given elsewhere (77). If we ignore the broadening attributable to thermal fluctuations, the main part of the spectrum will consist of a symmetric vibrational progression—superposed, probably, on the 1-0 band of an asymmetric vibration (vide infra)—and will in many respects resemble that of a diatomic molecule. Clearly if the vibrational constants (by which we mean to include the equilibrium internuclear distances) in the ground and excited states are the same, a single sharp set of lines would be observed. However, the greater the difference in these constants, the broader will the overall spectrum appear. Now the factor responsible for differences in the interactions of a given ion with its ligands is just the relative number of its e_g and t_{2g} electrons or, equivalently, the stabilization of the ion by the field in units of Dq. Bands for which both upper and lower states have the same number of t_{2g} electrons are therefore expected to be sharp, but those for which this number changes may be very broad.

For example, the lowest quartet-quartet transition of the $[Cr(H_2O)_6]^{+++}$ ion, which corresponds to $^4A_{2g} \rightarrow {}^4T_{2g}$ lies at 5800Å and has a half width of some 1625 cm^{-1} (53). The difference in crystal field stabilization between the two states is $10Dq$, which corresponds to the excitation $(t_{2g})^3 \rightarrow (t_{2g})^2(e_g)$. By contrast, certain doublet states, which arise from essentially the same ground $(t_{2g})^3$ configuration, are also seen in the spectrum. The bands, or rather lines, corresponding to these as the upper states of spin-forbidden systems in crystals are so sharp that Zeeman splittings of only 1 cm^{-1} or so are readily observed (88, 89). [These factors were recognized by Freed (34) and Van Vleck (102), but first correctly formalized by Orgel (77).]

Strong fields.—We now consider the case where the crystal field splitting parameter Dq is large enough so that the torques exerted on the orbital motions of the electrons are determined by the lattice site symmetry, rather than by the correlative interactions between them. The forces tending to repel the electrons of the central ion from the ligands cause a complete "Paschen-Back" effect which destroys the L, S coupling at the ion. In place of these quantum numbers, we now have the occupation numbers of the t_{2g} and e_g orbitals. The lowest group of states arises by filling first the t_{2g} shell

[9] The argument may also be given in terms of octahedral stabilization to which it is equivalent. One can see why the heats of hydration will not follow the Dq analysis exactly: for the different effective crystal radii will also imply different contributions from $\mathfrak{V}_R$ to the stability of the aquo complexes. The qualitative explanation is unaffected, however.

and only then, when six electrons have been accommodated, the less stable e_g levels. Such an assignment or crystal configuration will subsume a number of different states in cases of degeneracy, whose splitting is due to the coulomb repulsions of the electrons. These same repulsions are, of course, responsible for the separations of the different groups of multiplets in the spectrum of the free ion. In Table II, we list the lowest configurations and the crystal states into which they are split by the correlative interactions.

TABLE II

STATES AND ENERGIES IN STRONG OCTAHEDRAL FIELDS

Atomic Configuration	Crystal Configuration	Symmetry of Ground State	Octahedral Stabilization	Promotional Energy	Symmetries of Other States
d	(t_{2g})	$^2T_{2g}$	$4Dq$	0	—
d^2	$(t_{2g})^2$	$^3T_{1g}$	$8Dq$	$3F_2-15F_4$	$^1A_{1g}$, ^1E_g, $^1T_{2g}$
d^3	$(t_{2g})^3$	$^4A_{2g}$	$12Dq$	0	^2E_g, $^2T_{1g}$, $^2T_{2g}$
d^4	$(t_{2g})^4$	$^3T_{1g}$	$16Dq$	$6F_2+145F_4$	$^1A_{1g}$, ^1E_g, $^1T_{2g}$
d^5	$(t_{2g})^5$	$^2T_{2g}$	$20Dq$	$15F_2+275F_4$	—
d^6	$(t_{2g})^6$	$^1A_{1g}$	$24Dq$	$5F_2+255F_4$	—
d^7	$(t_{2g})^6(e_g)$	^2E_g	$18Dq$	$7F_2+105F_4$	—
d^8	$(t_{2g})^6(e_g)^2$	$^3A_{2g}$	$12Dq$	0	$^1A_{1g}$, ^1E_g
d^9	$(t_{2g})^6(e_g)^3$	^2E_g	$6Dq$	0	—

It will be noticed that, in every case, there is only one state of maximum multiplicity which, by Hund's principle, is therefore also the ground state. The multiplicities and symmetries predicted for these ground states are the same, both in the weak and strong field limits, for all cases except d^4, d^5, d^6 and d^7. This is due to the fact that, accidentally so to speak, the occupation numbers in the former limit differ appreciably from those in the latter only for these numbers of electrons. The total spin in the strong field limit is also uniformly lower—just as the octahedral stabilization is higher—in these cases. Thus the strong field limit refers to those complexes which, on the basis of his magnetic criterion, Pauling calls covalent (81).

The spectra of complexes whose ligands, such as the cyanide ion, give rise to strong fields are easily classified. In the d^2, d^3, d^4 and d^8 cases, there will be a number of spin-forbidden bands involving no change in crystal configuration; these bands should therefore be sharp, as is observed in complexes of Cr^{+++} (54). However, in the other cases, namely d^5, d^6, and d^7, the upper states of different multiplicity all involve at least one excitation $(t_{2g})^{-1}(e_g)$. Their spin-forbidden bands should therefore be broad; such a system has been described for diamagnetic Co^{+++} (54). Bands involving no spin change must all be accompanied by changes in crystal configuration and these are therefore uniformly broad.

The evaluation of the appropriate energies in the limit of strong fields is quite straight-forward.[10] These are listed for the ground states of the ions in the crystal, referring them to the ground states of the free ions. In general, the crystalline states in the strong field case are not stationary states of the free ion, but rather linear combinations of these, called valence states; their energies, apart from the crystal stabilization, are called promotional energies. Values for the parameters F_2, F_4 are obtained from the spectra of the free ions (28). Values of Dq, which depend both upon the nature of the ligands and the ions with which they complex, are generally determined semi-empirically. From Table II, quantitative criteria may be given to distinguish the weak from the strong field cases: for example, in the former limit, the field stabilization for d^6 ions is only $4Dq$; in the latter, however, it is as much as $24Dq$, but this has been achieved at the expense of some $5(F_2+51F_4)$ in promotional energy. When the last quantity is much greater than $20Dq$, the complex is paramagnetic and conversely when it is much less the complex is diamagnetic. Very frequently, the two crucial quantities are of comparable magnitude and these situations are treated in terms of intermediate coupling [Van Vleck (101), Howard (47), Kotani (60) and particularly Orgel (73, 76) who lists values of the parameters F_2, F_4, also Jørgensen (55) and Ballhausen (8). Valence states are reviewed by Moffitt (70)].

Fields of intermediate strength.—Although, as has been indicated, there may be discontinuities in the symmetries and multiplicities of the ground states of ions on going from the weak to the strong field case, the crystal field theory treats the transition domain in terms of the same physical picture—without explicitly invoking any discontinuous change in bond type. We shall illustrate the appropriate analysis, which deals with the intermediate coupling, for a particularly simple case, namely that of two d electrons, or of two holes in the completed d^{10} shell. For simplicity, we confine our attention to triplet states.

The free ions with configurations d^2 or d^8 have two triplet states, ^3F and ^3P, of which the former is more stable than the latter by some $15(F_2-5F_4)$ in both cases. Under the influence of a weak field, ^3F yields $^3A_{2g}$, $^3T_{2g}$ and $^3T_{1g}$ components, whereas the ^3P state is not split and transforms under $^3T_{1g}$. Since these are the only triplets that occur, we see that even in the strong field limit, the $^3A_{2g}$ and $^3T_{2g}$ states are correctly represented by their pure ^3F functions: these may also be written $(e_g)^2$ or $(t_{2g})^6(e_g)^2$ and $(t_{2g})(e_g)$ or $(t_{2g})^5(e_g)^3$ respectively. However, $^3F(T_{1g})$ and $^3P(T_{1g})$ may interact in stronger fields. That they will, in fact, do so is clear because the crystal field energy of the ground $^3T_{1g}$ state of d^2 is different in the two limits. A continuous change, with increasing Dq, will occur during which the $^3F(T_{1g})$ and $^3P(T_{1g})$ functions

[10] The octahedral field contributes terms which are just obtained by counting the numbers of electrons in the t_{2g} and e_g orbitals. The intra-atomic energies may be given in terms of Slater's F_2, F_4 parameters by the same methods as are used in atomic spectroscopy (28)—for the set of orbitals t_{2g}, e_g is just another listing of the usual atomic d orbitals.

are progressively contaminated by each other until finally, in the strong field limit, the eigenfunctions arise instead from the pure configurations $(t_{2g})^2$ or $(t_{2g})^4(e_g)^4$ and (t_{2g}) (e_g) or $(t_{2g})^5(e_g)^3$.[11]

We see that the transition between the strong and weak field cases—and therefore the compromise between correlative interactions, which are the basis of Hund's principle, and the tendency to minimize the crystal field energy—may be handled by the theory. And that a singlet state of d^6 should cross over several triplets and then the quintuplet ^5D state, the $^5T_{2g}$ component of which it usurps as the ground state of, for example, most Co^{+++} complexes, is no longer surprising and requires no special postulates other than a strong crystalline potential $\mathfrak{V}_O$.[12]

In order to illustrate the degree of accuracy that may be obtained in this way, let us consider the spectrum of the complex $[Ni(NH_3)_6]^{++}$ ion. This has three bands, whose maxima lie at 10,700, 17,500 and 28,100 cm^{-1} respectively (56). The only reasonable assignment for the first is $^3A_{2g} \rightarrow {}^3T_{2g}$, which has an excitation energy of $10Dq$ and does not depend on the separation of the ^3F and ^3P states of the free ion—some 15,800 cm^{-1} (72). We take $Dq = 1070$ cm^{-1}, therefore, together with the last figure and calculate the positions of the other two bands, which are both $^3A_{2g} \rightarrow {}^3T_{1g}$ transitions. In this way,[11] we find 17,600 cm^{-1} for the second band and 30,300 cm^{-1} for the third. The agreement with the experimental values seems to flatter somewhat the basic premises of the theory.

[Finkelstein & Van Vleck (33), Abragam & Pryce (4), Orgel (73, 75), Tanabe & Sugano (93, 94). For a very striking confirmation of the theory see Jørgensen (56), but also Owen (79).]

The spectrochemical series.—Many regularities in the spectra of octahedral complexes had been noted some time before the advent of crystal field theory. It was observed, for example, that the successive replacement

[11] The diagonal elements of the $^3T_{1g}$ part of the energy matrix, whose rows and columns refer to the weak field case, are clearly $[E^0 \mp 6\ Dq]$ and $[E^0 + 15(F_2 - 5F_4)]$, where E^0 is just the energy of the free ^3F ion in the spherically symmetric field $\mathfrak{V}_R$. The off-diagonal elements are found by noting that, as F_2, F_4 tend to zero, the eigenvalues must become those of the strong field limit, namely $\mp$ $8Dq$ and $\pm$ $2Dq$ respectively. With an appropriate phase choice, they are therefore $4Dq$ in both cases. Since $Dq > 0$ by our convention, the upper signs refer to the d^2 configuration and the lower to d^8.

[12] The analysis we have given could equally well be developed by starting with the configurational functions and making the transition in the other direction; the two methods are, of course, entirely equivalent. It is interesting to note that the average numbers n_t, $n_e = n - n_t$ of electrons in the t_{2g}, e_g orbitals are easily obtained for a particular state K of d^n by plotting its energy E_K as a function of Dq. Since E_K, for a given Dq, assumes a stationary value with respect to the coefficients of, say, the various configurational functions, we have

$$dE_K/d[Dq] = (\partial E_K/\partial [Dq])_{n_t} = -4n_t + 6n_e.$$

This formula is useful in discussing band widths [Orgel (76)].

of I^- by Br^-, Cl^- and H_2O as the ligands surrounding a particular cation shifted the maxima of prominent band systems to progressively shorter wave lengths. Similar effects were noticed with other ligands, and it appeared possible to classify these on the basis of their spectral effects. This led to the construction of the spectrochemical series [Fajans (32), Tsuchida (95, 96)]:

$$I^- < Br^- < Cl^- \lesssim OH^- < F^- \lesssim H_2O < \text{pyridine} < NH_3 < \text{ethylene diamine} < CN^-.$$

Minor variants arose, depending mainly on the particular cation in conjunction with which they were developed. But the general trend of the ligands appeared to be roughly independent of the central ion. The spectra concerned, it should be remarked, were those diffuse systems which we now classify as spin-allowed. With certain conspicuous exceptions, the qualitative features of a given cation could be systematized very satisfactorily in this way. Those ligand replacements which did not fall into line were accompanied by radical changes in stereochemistry or a change in multiplicity of the central ion.

By applying the spectrochemical series to, for example, the d^9 (Cu^{++}, say) case, we see that we may rationalize the ligand sequence as one of increasing Dq. The excitation energy is $10Dq$ here, and the hypsochromic shifts must therefore correspond to increases in this parameter. More generally, let us suppose that the series represents a succession of increasing octahedral fields $\mathfrak{V}_O$ when the relevant ligands are associated with a given central ion, whatever this may be. Let us further agree to consider only spin-allowed band systems. Then it may be proved that unless the multiplicity of the ground state changes, the spectrum of a given octahedral ion is shifted to shorter wave lengths on replacing its ligands by others lying above it in the spectrochemical series.

This "existence theorem" is easily established for magnetically normal complexes whose symmetry and spin for the ground states are those of the weak field limit.[13] In those cases, namely d^4, d^5, d^6 and d^7, where the ground state multiplicity is different in the strong and weak field limits, two quite distinct types of spectral behaviour may occur. For although the energy levels all move continuously as functions of Dq, as soon as, for example, the

[13] For the configurations d^1, d^5 and d^9, as well as for d and d^9, there is no distinction between the weak and strong field cases, since the free ions have only one, namely their ground state of maximum multiplicity. Their lower and upper states both arise from this term, and their separation is linear in Dq. The remaining ions, d^2, d^3, d^7 and d^8, have two states of maximum multiplicity, of which ^3F or ^4F is the ground state and ^3P or ^4P the excited state. In the weak field limit, the P states are not split but yield T_{1g} states. Their interactions with the ground states of d^2, d^7 for intermediate or strong fields can only depress the latter, so that the intervals, which increase linearly in both limits, increase more rapidly with Dq in the intermediate domain. And finally, for d^3 and d^8, whose ground states are the same in fields of all sizes, we have only to note that the excitation energies increase linearly in both limiting cases.

$^1A_{1g}$ state of Co^{+++} supplants its $^5T_{2g}$ state as the ground state, the selection rules change. No longer are the prominent bands in the spectrum due to quintuplet-quintuplet transitions, but singlet-singlets take their place. It is an entirely different set of states that is now "visible." A simplifying factor in this magnetically "anomalous" case arises from the fact that, in the strong field limit, the ground state is the only state of its total spin which arises from the lowest configuration. In this limit, or near it—and for present purposes all these "anomalous" cases fall into this category—, it is clear that an increase in Dq removes the ground state yet further from all other states of the same multiplicity, which must arise from excited crystal configurations: the existence of the spectrochemical series has been demonstrated for such complexes also.

It may be observed that the spectral shifts of different bands are governed by the same factor which accounts for their breadths. Analytically, both depend upon the quantity $d(\Delta E)/d(Dq)$.[12] Thus the absence of narrow spin-allowed bands and the existence of the spectrochemical series are closely related. Indeed, it is clear that the broader the band, the more it should be shifted on replacing the ligands by others near them in the spectrochemical series. However, it is only for the spin-allowed bands that the direction of the displacement is always the same. $d(\Delta E)/d(Dq)$ may be zero, or even negative and reverse this, for the spin-forbidden bands.

[General theories of colour have been given mainly by Orgel (73, 75, 77, 78) and by Tanabe & Sugano (93, 94). Other references are classified by the ions they consider most specifically: Ti^{+++}: Ilse & Hartmann (48); V^{+++}: Ilse & Hartmann (49); Cr^{+++}: Hartmann & Kruse (42); Mn^{++}: Schläfer (87); Co^{+++}: Basolo, Ballhausen & Bjerrum (12); Co^{++}: Abragam & Pryce (4), Ballhausen & Jørgensen (7); Ni^{++}: Hartmann & Fischer (41), Ballhausen (6, 10), Jørgensen (56); Cu^{++}: Abragam & Pryce (3), Bjerrum, Ballhausen & Jørgensen (17), Ballhausen (5).]

Spin-orbit coupling.—Systems with perfect octahedral symmetry are rarely, if ever, discovered. However, in order to understand magnetic effects in solids, it is most illuminating to see how the spin-orbit coupling changes on going from the free ion, first to a site subject to strong fields of this ideal kind.

The interaction of the spins of a system of d electrons with their own orbital motions in a central force field may be written

$$\mathcal{H}_\zeta = \zeta_d \sum_i \mathbf{l}_i \cdot \mathbf{s}_i,$$

where ζ_d is a characteristic of the radial part of the d orbitals and of the central field; $\boldsymbol{l}_i$, $\boldsymbol{s}_i$ are supposed, throughout, to be expressed in units of $\hbar$. The same form for the spin-orbit interaction operator will also be used for the crystalline ions, though this involves an additional assumption. When L, S are good quantum numbers—e.g., for the free ion in Russell-Saunders coupling and for the weak field limit—, it is easy to show that $\mathcal{H}_\zeta = \lambda \boldsymbol{L} \cdot \boldsymbol{S}$, where λ, whose value depends on the particular L, S term considered, is

a simple fraction of ζ_d; ζ_d is always positive, though λ need not be so. For the free ion, $\boldsymbol{S}$ and $\boldsymbol{L}$ couple to form a resultant J, of course, where the different values of $J=|L-S|, \cdots, L+S$ represent the individual multiplets. Their energies due to the spin-orbit coupling are given by the Landé rule, namely, $\frac{1}{2}\lambda[J(J+1)-L(L+1)-S(S+1)]$. Values of λ are generally around ± 100 cm^{-1}, though they are appreciably larger for Ni^{++} (-335 cm^{-1}) and for Cu^{++}(-828 cm^{-1}). Moreover, for ground states, it changes sign on going from a less to a more than half-completed shell: "holes" have positive charges.

It is easy to see by symmetry arguments which crystal states will show first-order multiplet separations. The orbital angular momentum operator transforms under T_{1g} of the group O_h. Accordingly, a term whose orbital symmetry is Γ, say, will exhibit properties of angular momentum and therefore propensities for spin-orbit coupling only if the direct product representation $\Gamma \times T_{1g} \times \Gamma$ contains the identity A_{1g}. It follows that the multiplet structure is expected to be pronounced only for those octahedrally coordinated ions with either T_{1g} or T_{2g} ground states.[14]

In order to illustrate the very striking changes which may occur on first tying $\boldsymbol{L}$ to the octahedral lattice and only afterwards allowing it to couple with $\boldsymbol{S}$, we take the case of a single d electron. The free ion has states $^2D_{3/2}$, $^2D_{5/2}$ with spin-orbit energies of $-(3/2)\zeta_d$ and ζ_d respectively. However, on placing this in the strong field, we obtain the sixfold $^2T_{2g}$ and fourfold ^2E_g levels. We label the possible functions $t_{2g}{}^0$, $\bar{t}_{2g}{}^0$, $e_g{}^\alpha$ and so on, the bars over orbital symbols denoting that they are to be taken with β spin, and their absence showing α spin.

Remembering that $m=m_s+m_l$ is a good quantum number for the free atom, we see that the only interactions which occur under $\mathcal{H}_\zeta$, within the $^2T_{2g}$ manifold, are of $t_{2g}{}^0$ with $\bar{t}_{2g}{}^-$ and of $\bar{t}_{2g}{}^0$ with $t_{2g}{}^+$. The four ^2E_g's do not interact with each other at all. As a result, no splitting and no contribution to the energy of the ^2E_g state occurs—as had been anticipated. On the other hand, it is found that the $^2T_{2g}$ state is split into a doubly-degenerate level, $^2T_{2g}{}^7$ say, and a fourfold level $^2T_{2g}{}^8$. Their energies are ζ_d and $-\frac{1}{2}\zeta_d$ respec-

[14] The qualitative aspects of the multiplet structure are most easily seen by group theory also. In order to account for systems with an odd number of electrons, the octahedral group is replaced by the corresponding "double group," which contains the element R—a rotation through 2π about an arbitrary axis. In this way the representations of the simple group are augmented by certain double-valued representations, under which systems of odd spin transform. The symbol $^2T_{2g}$ now signifies a direct product representation of the double group, whose elements will act simultaneously on both space and spin variables; its irreducible components are called Γ_7 and Γ_8 by Bethe (15). Thus the degenerate $^2T_{2g}$ term is split into two levels by $\mathcal{H}_\zeta$, one of which is doubly-degenerate, namely $^2T_{2g}{}^7$, the other being the fourfold $^2T_{2g}{}^8$ state. On the other hand, the fourfold degeneracy of the ^2E_g term is not removed, its Γ_8 character being specified by the symbol $^2E_g{}^8$. It may be noticed that $^2E_g{}^8$ may interact, though it is not split, in second-order of $\mathcal{H}_\zeta$, with $^2T_{2g}{}^8$, but not with $^2T_{2g}{}^7$.

tively, so that $^2T_{2g}{}^8$ is the lower multiplet; its eigenfunctions are

$$t_k{}^8 = \frac{1}{\sqrt{3}}(\sqrt{2}l_{2g}{}^0 + \bar{l}_{2g}{}^-), \qquad t_l{}^8 = \frac{1}{\sqrt{3}}(-\sqrt{2}\bar{l}_{2g}{}^0 + l_{2g}{}^+),$$
$$t_m{}^8 = \bar{l}_{2g}{}^+, \qquad t_n{}^8 = l_{2g}{}^-.$$

Those for the upper $^2T_{2g}{}^7$ state are just

$$t_a{}^7 = \frac{1}{\sqrt{3}}(l_{2g}{}^0 - \sqrt{2}\bar{l}_{2g}{}^-), \qquad t_b{}^7 = \frac{1}{\sqrt{3}}(\bar{l}_{2g}{}^0 + \sqrt{2}l_{2g}{}^+).$$

The splittings are shown in Figure 1.

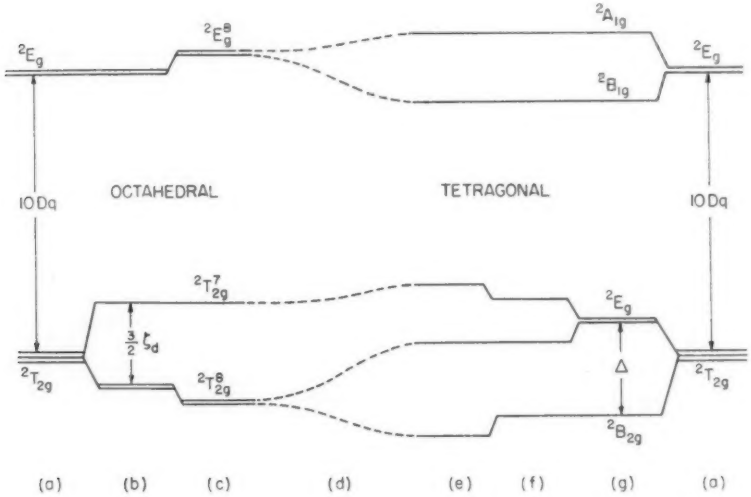

FIG. 1. Term splittings for a single *d* electron. (Each line represents a spin doublet.)
(a) Levels in a strong octahedral field,
(b) ..... with weak spin-orbit coupling,
(c) ..... with stronger spin-orbit coupling.
(g) Levels in strong octahedral and weak tetragonal fields,
(f) ..... with weaker spin-orbit coupling,
(e) ..... with spin-orbit coupling and tetragonal fields of comparable size.
(d) ..... Intermediate domain.

To cover the intermediate range, where spin-orbit coupling becomes stronger and eventually supplants the octahedral field in directing $\boldsymbol{L}$, it may be noted that each of the $^2T_{2g}$ states interacts with one of the ^2E_g states under $\mathcal{H}_\zeta$—and these are the only further interactions that occur. Since the four off-diagonal elements concerned are all equal to $\sqrt{(3/2)}\cdot\zeta_d$, no splitting,

but only a uniform displacement of all the four states occurs until, finally, when ζ_d overwhelms Dq, the free ion functions are recovered and J is a good quantum number again. To the first order in the parameter $(\zeta_d/10Dq)=\xi$, say, the perturbed functions for the lowest multiplet are typified by

$$t_m^3 - \sqrt{(3/2)}\cdot\xi e_g^a.$$

The second-order energy correction for this level is just $-(3/2)\zeta_d^2/10Dq$.

The most interesting features of these results appear when we consider the Zeeman splittings. In a magnetic field $\boldsymbol{H}$, the additional term

$$\mathcal{H}_M = \beta\boldsymbol{H}\cdot\sum_i(\boldsymbol{l}_i + 2\boldsymbol{S}_i) = \beta\boldsymbol{H}\cdot(\boldsymbol{L}+2\boldsymbol{S})$$

must be added to the Hamiltonian. The separations within a given multiplet due to the field along some axis κ, say, may be expressed in the form $g_\kappa\beta H_\kappa$, where β is the Bohr magneton and g_κ the so-called spectroscopic splitting factor. For free ions, it is well known that

$$g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)},$$

whenever Russel-Saunders coupling holds. The g-factors are also isotropic—that is independent of the orientation of κ—for ions in octahedral sites. However, their values differ widely from those given by the Landé formula.

Evaluating (L_z+2S_z) using the unperturbed eigenfunctions for $^2T_{2g}{}^7$, we see that its levels are separated by just $2\beta H_z$ and therefore that $g=2$. Similarly, the ^2E_g levels are split into two doublets of energy $\pm\beta H_z$, magnetic dipole transitions being allowed only between and not within them; once again, $g=2$. The "spin-only" values are obtained in both cases. However, the $^2T_{2g}{}^8$ quartet is not split by the field at all, using zeroth-order functions.[15] Its g-factor differs from zero only by virtue of its "high frequency" terms, coupling it to the ^2E_g state. Under these conditions, it gives an undisplaced doublet, within which magnetic dipole transitions are forbidden, and two singlets to which they may make transitions. Since the latter have excitation energies $\pm 4\xi\beta H_z$, we see that $g=4\xi$ for $^2T_{2g}{}^9$; because ζ_d is of order 100 cm^{-1}, but $10Dq$ is around 20,000 cm^{-1}, the g-factor is in any case rather small. By comparison, the g-factors are 4/5 and 6/5 for the $^2D_{3/2}$ and $^2D_{5/2}$ levels of the free ion.

It is easy to treat the complementary case of a single hole in a completed d^{10} shell. Here the free ^2D ion has an inverted multiplet structure, with $^2D_{5/2}$ $(-\zeta_d,\ g=6/5)$ and $^2D_{3/2}([3/2]\zeta_d,\ g=4/5)$. By definition, ζ_d and Dq remain positive, as does ξ therefore. Now ^2E_g is the ground state of the crystal and, in a perfectly octahedral field, it is four-fold degenerate. If we include cor-

[15] The way in which the precessional motion of $\boldsymbol{L}$ is anchored to the crystal lattice in these complexes has an illuminating parallel in diatomic spectroscopy. In the NO molecule, for example, the orbital angular momentum is partially quenched by the strong axial fields, so that it has no perpendicular components in, say, its $^2\Pi$ ground state. The lower $^2\Pi_{1/2}$ component also has a vanishing g-factor.

rections for its interactions with the ${}^2T_{2g}{}^3$ state, its eigenfunctions are typified by

$$e_g{}^b + \sqrt{(3/2)} \cdot \xi t_k{}^3.$$

In the presence of a magnetic field, the degeneracy is completely removed; the displacements are $\pm\beta H_z$ and $\pm\beta(1+4\xi)H_z$ respectively. By the selection rule $\Delta m = \pm 1$, we see that the corresponding g-factors are 2 and $2(1+4\xi)$.

To summarize, it is only the ions whose ground states in the crystal have orbital symmetry T_{1g} or T_{2g} which show large multiplet separations. The appropriate g-factors, and therefore also the bulk magnetic properties, will differ widely from those of the free ion. Other states, whose orbital degeneracy, if any, is only of the twofold E_g variety, show at best only second-order splittings. Their g-factors are close to the "spin-only" value of 2, or rather 2.0023 as given by quantum electrodynamics.

Fields of Lower Symmetry

There are, of course, many complexes whose symmetry is not octahedral. Indeed, the more sensitive one's measurements, the farther must one go to find a perfectly octahedral system. Even when the six ligands are identical, there are many factors tending to destroy their most regular arrangement about the cation. Crystals show, to a greater or lesser degree, both optical and magnetic anisotropies. This makes it very important to discuss the effects of departures from octahedral symmetry.

Tetragonal fields.—Consider, first, the case of a complex containing four identical ligands arranged in a square, at whose centre the cation is located. Immediately above and below it, two other ligands are placed: $[MX_4Y_2]$. The symmetry is now that of a distorted octahedron, namely D_{4h}. Examples of this are *trans*-$[CO(NH_3)_4Cl_2]^+$, or just $[H_2O \cdots Cu(H_2O)_4 \cdots OH_2]^{++}$ where two waters of crystallization are less closely coordinated to the central ion than are the other four. The most general potential is easily seen to be $(\mathcal{V}_R+\mathcal{V}_O+\mathcal{V}_T)$, where

$$\mathcal{V}_T = \sum_i \{\mathcal{Y}_{20}(\theta_i, \phi_i)\mathcal{R}_2(r_i) + \mathcal{Y}_{40}(\theta_i, \phi_i)\mathcal{R}_4'(r_i)\}.$$

We shall study the complex as if it were octahedral, say $[MX_6]$, and then add the tetragonal perturbation $\mathcal{V}_T$, whose effect is generally small with respect to that of $\mathcal{V}_O$. $\mathcal{V}_T$ will have the sense either of attracting or of repelling electrons in the neighbourhood of the ligands Y. If Y lies below X in the spectrochemical series, we should expect this to be an attraction.

Now suppose we have just one electron in this field. It is clear that the unstable e_g orbitals are split by $\mathcal{V}_T$ and span a_{1g} and b_{1g} of D_{4h}; their energies may be written

$$\epsilon[e_g{}^a(a_{1g})] = \epsilon_0 + 6Dq - 2Ds - 6Dt,$$
$$\epsilon[e_g{}^b(b_{1g})] = \epsilon_0 + 6Dq + 2Ds - Dt;$$

Ds, Dt are splitting parameters for $\mathcal{Y}_{20}$, $\mathcal{Y}_{40}$ respectively, in the same way that

Dq is for $\mathcal{V}_O$. Similarly, the lower three levels split into a doubly-degenerate e_g pair and a single b_{2g} level of D_{4h}:

$$\epsilon[t_{2g}^{\pm}(e_g)] = \epsilon_0 - 4Dq - Ds + 4Dt$$
$$\epsilon[t_{2g}^{0}(b_{2g})] = \epsilon_0 - 4Dq + 2Ds - Dt.$$

For the moment, we suppose Ds, Dt to be large with respect ot ζ_d.[16]

To see how these splittings affect a polyelectronic system, let us consider the spectra of diamagnetic Co^{+++} complexes, which may be treated with reasonable accuracy using the strong field approximation. The ground $^1A_{1g}$, $(t_{2g})^6$ state is non-degenerate, but the excited $^1T_{1g}$ and $^1T_{2g}$ states arising from the configuration $(t_{2g})^5(e_g)$ are split by the field: formally, $^1T_{1g}$ becomes $^1A_{2g}+{}^1E_g$ and $^1T_{2g}$ becomes $^1B_{2g}+{}^1E_g$ on going from O_h to D_{4h}. Owing to the electronic repulsions, $^1T_{2g}$ lies some $16(F_2-5F_4)$ above the lower excited $^1T_{1g}$ state.[17] Using the individual orbital levels which we have already evaluated, it may then be shown that the separation of the levels arising from the $^1T_{1g}$ state is

$$E[^1T_{1g}(A_{2g})] - E[^1T_{1g}(E_g)] = (35/4)Dt,$$

whereas the similar splitting of the $^1T_{2g}$ levels follows

$$E[^1T_{2g}(E_g)] - E[^1T_{2g}(B_{2g})] = 6Ds - (5/4)Dt.$$

Since the longer wavelength band system, $^1A_{1g} \rightarrow {}^1T_{1g}$, is of some further interest, we note that if Y, say Cl^-, is lower down in the spectrochemical series than X, say NH_3, then $Dt>0$, for $\mathcal{V}_T$ will stabilize the a_{1g} orbital. In this case, we should expect the band to be split, the shorter wave-length component being due to an upper state of symmetry A_{2g} in D_{4h}.

Spectroscopic splitting factors.—In order to illustrate the magnetic behaviour of ions in fields of distorted octahedral symmetry, we refer again to the case of a single d electron and to a single hole. To avoid further notational difficulties, we assume the symmetry to be tetragonal (D_{4h}) and throughout label orbitals according to their species symbols in this lower group.

We first examine the Ti^{+++} ion in such fields, taking $(5Dt-3Ds)=\Delta$, say, to be positive. Of the three orbital levels arising from the octahedral $^2T_{2g}$ term, b_{2g} is the lowest, the doubly-degenerate e_g levels lying some Δ above it. If ζ_d is very small, it is clear that spin-orbit coupling is only ap-

[16] It may be noticed that since the effect of all odd-order potentials vanishes in a representation containing only d electrons, certain curious features emerge. Without including higher configurations, it will never be possible to localize electrons on one side of an axis containing the cation, since the functions concerned are all of even parity. Thus the replacement of only one of the ligands of $[MX_6]$ by Y would have to be described by means of the same potential $\mathcal{V}_T$—or rather, one half of it—that determines the perturbation on forming *trans*-$[MX_4Y_2]$. A molecule of symmetry C_{4v}, like $[MX_5Y]$, would appear to have the higher symmetry D_{4h}.

[17] This is shown most easily by evaluating the energies of the two unique configurations $(e_g)^4(b_{2g})(b_{1g})$, $^1T_{1g}(A_{2g})$ and $(e_g)^4(b_{2g})(a_{1g})$, $^1T_{2g}(B_{2g})$. The concomitant splittings under $\mathcal{V}_T$ are obtained by an obvious extension of this.

preciable in the upper two levels (see figure). However, it will more often be the case that ζ_d and Δ are comparable (around 100 cm^{-1}), though both are small with respect to $10Dq$. We now find that b_{2g} mixes with $\bar{e}_g^-$, the energy difference between the two unperturbed levels being $(\Delta+\frac{1}{2}\zeta_d)$; their off-diagonal element in $\mathcal{H}_\zeta$ is $-(1/\sqrt{2})\zeta_d$. Similarly, $\bar{b}_{2g}$ and e_g^+ mix. The resulting eigenfunctions for the perturbed ground state, a Kramers spin doublet, take the forms $(Cb_{2g}+De_g^-)$, $(C\bar{b}_{2g}-De_g^+)$, where C and D are simple functions of ζ_d, Δ. Finding expectation values for (L_z+2S_z) and for (L_x+2S_x), their Zeeman splittings may be written $g_\parallel\beta H_z$ and $g_\perp\beta H_x$ respectively, for magnetic fields directed along, or normal to the four-fold axis. Explicitly,

$$g_\parallel = -1+3(\Delta+\tfrac{1}{2}\zeta_d)/\sqrt{(\Delta+\tfrac{1}{2}\zeta_d)^2+2\zeta_d^2},$$

$$g_\perp = 1+(\Delta-\tfrac{1}{2}\zeta_d)/\sqrt{(\Delta+\tfrac{1}{2}\zeta_d)^2+2\zeta_d^2}.$$

These reduce to 0, of course, when $\zeta_d \gg \Delta$, for the tetragonal perturbation is then suppressed and the effective symmetry is octahedral again: the levels reduce to components of $^2T_{2g}{}^8$. On the other hand, if $\Delta \gg \zeta_d$, $g_\parallel$ and $g_\perp$ both become 2, and the orbital angular momentum is completely quenched in this state. The alum, $CsTi(SO_4)_2\cdot 12H_2O$, which has been studied by paramagnetic resonance (23), has trigonal, rather than tetragonal symmetry; but the qualitative splitting of the octahedral $^2T_{2g}$ state is exactly the same, as are the theoretical expressions for $g_\parallel$, $g_\perp$ to this approximation (18). Experimentally, it is found that $g_\parallel=1.25$ and $g_\perp=1.14$. The low figures are to be expected on the basis of the simple formulae, but their actual values require a more detailed discussion, in which second-order corrections arising from the excited octahedral ^2E_g state are taken into account.

Let us now take a single d hole, say, a Cu^{++} ion in a field corresponding to an octahedron which is elongated along the four-fold axis. Such fields occur in the Tutton salts and probably also in the hydrated ion. They stabilize electrons in the a_{1g} orbital, particularly, and accordingly repel holes there. We shall talk of orbital levels as occupied by holes. The lowest octahedral ^2E_g state is therefore split, b_{1g} being more stable than a_{1g}.[18] Unlike the case considered above, however, both b_{1g} and a_{1g} levels are magnetically inert so far as their orbital parts are concerned, and they do not interact under $\mathcal{H}_\zeta$. As in the octahedral case, these levels only interact in second-order of $\xi=\zeta_d/10Dq$, namely with the octahedrally excited $^2T_{2g}{}^8$ state (since both λ and $\mathcal{V}_O$ change sign when applying to holes, ξ remains positive). The perturbed eigenfunctions turn out to be

$$b_{1g}' = b_{1g}+\xi\left(b_{2g}+\frac{1}{\sqrt{2}}\bar{e}_g^-\right), \qquad \bar{b}_{1g}' = \bar{b}_{1g}-\xi\left(\bar{b}_{2g}-\frac{1}{\sqrt{2}}e_g^+\right)$$

for the lowest doublet; the e_g, b_{2g} orbitals prefaced by the parameter ξ refer

[18] The possibility that a_{1g} lies below b_{1g}—which seems physically unreasonable—is excluded by these measurements for, on this basis, we should have found $g_\parallel=2$, $g_\perp=2(1+3\xi)$.

to tetragonal levels of the excited octahedral $^2T_{2g}$ state. Correspondingly, the g-factors are

$$g_{\parallel} = 2(1 + 4\xi), \qquad g_{\perp} = 2(1 + \xi).$$

From low temperature resonance spectra (20), their values are found to be 2.4, 2.1 respectively (on correcting for slight rhombic distortions), in admirable accord with the theory if $\xi = 0.05$. On a quantitative basis, and this is rather typical, the agreement is less satisfactory: taking $\lambda = -828$ cm^{-1}, one would predict the maximum of the optical spectrum to lie around 16,600 cm^{-1} (3). In fact, the broad system observed in the spectrum of the aqueous ion has a maximum at 12,500 cm^{-1} (17), and shows no bands in the expected region. It appears, therefore, that in order to account for the g-factors one must assume that the spin-orbit coupling constant ζ_d ($= -\lambda$, here) is diminished from its free ion value to only about 625 cm^{-1} for the crystalline ion.

Paramagnetic resonance work serves to confirm the simple generalizations with which we began this particular discussion. Salts with $^{4,3}A_{2g}$ ground states, like Cr^{+++} and Ni^{++}, have g-factors reasonably close to the spin-only value ($g = 2 \pm 36\lambda/25Dq$)—closer than Cu^{++} for which ζ_d is remarkably large. Owing to the change from normal to inverted multiplet structure for the free ions, g is less than 2.0023 for Cr^{+++} and V^{++}, but larger for Ni^{++}. Moreover, since the orbital ground states are non-degenerate, unlike the ^2E_g state of Cu^{++}, the g-factors are very nearly isotropic. Contrastingly, Co^{++} salts whose crystal states arise from $^4T_{1g}$, show their orbital angular momenta very strongly. Similarly, since they are susceptible to, for example, tetragonal distortions, their g-factors are highly anisotropic ($g_{\parallel} = 5.5$ to 7, $g_{\perp} = 2.5$ to 3.5).

Studies of these microwave spectra yield very detailed information about the lowest energy levels. Higher order spin-orbit interactions together with intraionic spin-spin coupling terms—factors which had been predicted on the basis of low temperature susceptibilities and relaxations, for example, by Van Vleck and Penney (99)—are seen very strikingly. They help in the interpretation of the specific heats at very low temperatures. The resonance spectra also often show well defined hyperfine structures. Quite apart from the useful information about nuclear moments that these provide, illuminating if occasionally puzzling facts are disclosed about the more intimate details of the electronic eigenfunctions. These are of equal interest both for valence theory and for the theory of atomic spectra.

[Sources for magnetic theory are Van Vleck (97, 106) and Casimir (26); for paramagnetic relaxation Gorter (38) and Cooke (29); for paramagnetic resonance Abragam & Pryce (2), Bleaney & Stevens (22) and Bowers & Owen (24).]

Spectral intensities.—By many standards, the electronic absorption bands responsible for the colours of the transition-metal complexes would be regarded as very weak: the broad, spin-allowed systems which we consider

in these paragraphs have molar extinction coefficients which rarely exceed 100. On the other hand, many of these complexes appear to have centres of symmetry and, since no change in parity accompanies the excitations, these should be strongly forbidden, orbitally, in electric dipole radiation fields. It is perhaps even surprising that the oscillator strengths f of the main bands in the hexammines of Cr^{+++} and Co^{+++}, for example, should be as high as the 10^{-3} or so which are observed. The source of this intensity has been discussed several times, and two sets of explanations have been put forward. On the one hand, it is accepted that the symmetry has a centre of inversion (holohedral field), in which case the absorption probabilities are attributed either to magnetic dipole or to electric quadrupole radiation. Alternatively, it is supposed that a predominantly holohedral field is subject to hemihedral distortions arising either from the intimate properties of the static crystal field or from the vibrations of the ligands.

The former set are easily rejected in the present case, though they may be important in the spectra of rare earth salts. We observe that the orbital magnetic moments transform under T_{1g} of O_h, whereas the electric quadrupole tensor spans irreducible representations E_g and T_{2g} of this group. Now, for example, the 4750 Å ($^1A_{1g} \rightarrow {}^1T_{1g}$) and 3400 Å ($^1A_{1g} \rightarrow {}^1T_{2g}$) systems of $[Co(NH_3)_6]^{+++}$ are almost equally strongly absorbing (67). $^1A_{1g} \rightarrow {}^1T_{1g}$ is allowed for magnetic dipole, but forbidden in electric quadrupole radiation fields; the opposite holds for the second system: neither effect may separately account for the intensity of both band systems. Both are also too weak. Thus, on the basis of the magnetic dipole hypothesis, we should predict oscillator strengths of $(h\nu/6m_e c)\Sigma|\boldsymbol{L}|^2$, where m_e is the electronic mass and $\Sigma|\boldsymbol{L}|^2$ refers to the sum of the squares of the changes in angular momentum (in units of $\hbar^2$), on going from $^1A_{1g}$ to each of the $^1T_{1g}$ components. For diamagnetic cobaltic complexes of this kind, $\Sigma|\boldsymbol{L}|^2 = 24$ in the strong field approximation, so that the computed f is about 2×10^{-5}. The observed 10^{-3} is quite inexplicable on such a basis and, as it turns out, even less so for the $^1A_{1g} \rightarrow {}^1T_{2g}$ system assuming electric quadrupole radiation.

The considerably stronger absorption of bands in, for example, *cis*-$[Co(en)_2Cl_2]^+$ than in their *trans*-analogue (12) shows that static hemihedral fields are a major factor in promoting the intensities of bands. But this seems unlikely to be the only factor. The oscillator strengths of the halogenopentammines of Cr^{+++} and Co^{+++} are larger, but not inordinately so than those of the corresponding hexammines (67, 68): it is a little difficult to believe that slight but permanent hemihedral distortions of the crystal fields in the latter should have as profound an effect as the substitution of an NH_3 by a Cl^- ligand.[21]

It appears, therefore, that the influence of asymmetric vibrational modes must account for the observed intensities of symmetric ions like the hexammines. The mechanics may be seen as follows. Suppose Q represents a normal coordinate for a particular asymmetric vibrational mode of odd parity. The instantaneous crystal field has the form $(\mathcal{V}_R + \mathcal{V}_O + Q\mathcal{V}_Q)$, where $\mathcal{V}_Q$ is made

up of odd-order harmonics, and represents the momentary distortion of what we have supposed to be a perfect octahedron. Since the electronic motions respond almost immediately to the nuclear motions, we see that the eigenfunctions for the ionic electrons will be functions of Q which take the form

$$\psi(Q) = \phi_g + cQ\phi_u.$$

ϕ_g represents the electronic eigenfunction in the undistorted field, its parity being g. In the asymmetric nuclear configuration, $\mathcal{V}_Q$ causes ϕ_g to interact with excited states ϕ_u of odd parity—particularly those corresponding to one-electron jumps $(3d)^{-1}(4p)$. For simplicity, let us suppose Q to represent the only vibrational mode, the corresponding harmonic oscillator functions being χ_p, χ_q for quantum numbers p, q respectively. Then the electronic and vibrational (therefore, "vibronic") state of the octahedral complex is represented by a function $\Psi_p = \psi\chi_p$. If the force constants for this vibration are the same both in the electronic ground state N and in an excited state, V say, then the probability of a transition from Np to Vq is proportional to

$$|\boldsymbol{R}_{Np,Vq}| = \int\int \Psi_{Np}^{*}\boldsymbol{R}\Psi_{Vq}dvdQ|^2,$$

where $\boldsymbol{R}$ represents the electric dipole operator. We find that

$$\boldsymbol{R}_{Np,Vq} = \int (c_N^{*}\phi_{Nu}^{*}\boldsymbol{R}\phi_{Vg} + c_V\phi_{Ng}^{*}\boldsymbol{R}\phi_{Vu})dv \int \chi_{Np}^{*}Q\chi_{Vq}dQ,$$

from which we see that transitions are allowed only if the vibrational states p, q differ by one quantum. At low temperatures, therefore, the spectrum will correspond to the 1-0 band, the 0-0 band being absent. It may be noted that the vibrational integral is proportional to the square root of p or q, whichever is the greater. At higher temperatures, therefore, the stronger 2-1, 3-2, $\cdots$ bands appear, corresponding to larger amplitudes of vibration and greater hemihedral distortions, and the total intensity of these electronically forbidden systems increases.[19]

Of the various vibrations the complex may undergo, we should expect the asymmetric stretching modes to be more effective in breaking down the electronic selection rules than the weaker bending modes. There is only one such mode for an octahedral $[MX_6]$ complex, namely τ_{1u} (small Greek letters are used to denote vibrational species which transform under the representation whose symbol, like T_{1u}, is obtained from them by using Roman capitals). The selection rules are found by applying symmetry arguments to the vibronic functions Ψ, rather than to the ϕ's alone. $\chi_0(\gamma)$ belongs to the A_{1g} species and $\chi_1(\gamma)$ to the Γ species. Thus $\phi(^1A_{1g})\chi_0(\tau_{1u})$ combines with $\phi(^1T_{1g})\chi_1(\tau_{1u})$ in electric dipole radiation fields (T_{1u}) because $(A_{1g}\times A_{1g})$

[19] In general, the force constants for Q will not, of course, be the same in both states, nor may we neglect other modes; however, a more exhaustive treatment leads to very similar conclusions and encounters difficulties of notation alone.

$\times T_{1u}\times(T_{1g}\times T_{1u})$ contains the identity representation. Unfortunately, for purposes of assignments, the former also combines with $\phi(^1T_{2g})\chi_1(\tau_{1u})$, which means that one cannot in this way identify the upper state symmetries unambiguously.

Let us, as a specific illustration of these principles, consider the diamagnetic complex ions *trans*-$[Co(en)_2Cl_2]^+$ and *trans*-$[Co(en)_2Br_2]^+$. These are essentially tetragonal and almost identical, spectroscopically, with their tetrammine analogues (12). The perchlorates crystallize in the monoclinic system, whose *a*-axes are almost coincident with the fourfold axis of the complex ions, and whose *b*-axes are almost normal to this axis. As we have seen, the octahedral $^1A_{1g}\rightarrow{}^1T_{1g}$ system should be split into two bands, that to the red having an upper ^1E_g state, and that to the blue having $^1A_{2g}$. The crystals have been studied using polarized light, and two bands are in fact observed in the requisite regions (e.g., at 6200 Å and 4300 Å in the one case). The longer wave-length system absorbs more strongly with the electric vector along the *a*-axis, though it also absorbs appreciably when this vector lies along the *b*-axis. The band to the blue, on the other hand, disappears almost entirely when the electric vector lies along the *a*-axis, but is reasonably strong for the other orientation (109). The electric vector along the *a*-axis transforms like A_{2u}, whereas when it is normal to this it transforms under E_u of D_{4h}. Applying our analysis, we see that $^1A_{2g}$ can be seen in absorption only with the simultaneous excitation of α_{1u} (*a*-axis) or of ϵ_u (*b*-axis) vibrational modes. Transitions to the ^1E_g state, however, may occur with the aid of ϵ_u (*a*-axis) or of α_{1u}, α_{2u}, β_{1u} or β_{2u} (*b*-axis) excitations. As it happens, there are no vibrations of species α_{1u}, neither stretching nor bending modes, but there are stretching modes of species α_{2u} and ϵ_u. Thus $^1A_{1g}\rightarrow{}^1A_{2g}$ should appear for *b*-axis polarization alone, whereas $^1A_{1g}\rightarrow{}^1E_g$ should be active for both orientations (all upper states being derived from the same octahedral $^1T_{1g}$ term, of course). It follows that the upper state of the shorter wavelength system must be $^1A_{2g}$, in complete agreement with predictions based on the spectrochemical series.

[Herzberg & Teller (46), Van Vleck (102), Broer, Gorter & Hoogschagen (25), Ballhausen (9), Ballhausen & Moffitt (11).]

The Jahn-Teller effect.—As a general rule, it is found that those transition-metal ions whose ground states in octahedral fields are orbitally degenerate, form complexes whose symmetry is lower, say tetragonal or rhombic. This may be due to many causes: crystal packing considerations for the complex within a lattice, repulsions between neighbouring ligands and so forth. However, it is also to be expected on very general grounds which seem to be of some importance to their chemistry. According to a theorem of Jahn and Teller, when the orbital state of an ion is degenerate for symmetry reasons, its ligands will experience forces distorting the octahedron until they assume a configuration, both of lower symmetry and of lower energy, thereby resolving the degeneracy.

The physical background for this may be seen very readily. Consider once

more the case of a single d electron, or of a single hole, in a perfectly octahedral field. Let the two ligands on the z-axis move an equal distance S away from each other along their line of centres. At the same time, each of the other four ligands may be supposed to approach the central ion a distance $\frac{1}{2}S$, so that the net displacement is orthogonal to a totally symmetric expansion of the octahedron. The electrons of the ion are now in a crystal field which, to a first approximation, may be written $(\mathcal{V}_R+\mathcal{V}_O+S\mathcal{V}_T)$, where $\mathcal{V}_T$ describes the effect of the tetragonal distortion, per unit distance, and is independent of S. We have already seen that the degeneracy is at least partially removed in such fields. The d, $^2T_{2g}$ state splits into an orbital singlet and doublet, whereas d^9, ^2E_g splits into two orbital singlets; moreover, the splitting is linear in S. The total energy of the ground state therefore also contains terms linear in S and cannot represent a stable configuration, not being minimal with respect to this parameter: the ligands may be regarded as experiencing a set of non-totally symmetric forces which destroy their octahedral arrangement. Ultimately, an equilibrium configuration of lower symmetry is attained, whose geometry is determined by including quadratic and higher powers of the displacement coordinates in the energy expression.[20]

A rather curious but characteristic effect arises occasionally, not only for complexes of this kind but also in quite different molecular systems such as the cyclopentadienyl radical. It may show itself when the displacement S is a member of a degenerate set of symmetry coordinates for the undisplaced configuration. The case we have chosen illustrates this since S, together with another displacement S' span E_g of the octahedral group. In the latter, the two ligands on the y-axis approach, and the two on the x-axis move away from the central ion equal distances $\sqrt{3}\cdot S'$. Let us write $S=R\cos\chi$, $S'=R\sin\chi$. Then, by considering quadratic and higher terms in the energy, it is sometimes found that whereas R is strongly determined by the minimum energy requirement, the "phase" χ is only weakly determined—that is, it is almost a cyclic coordinate which does not appear in the potential energy expression. There exists a continuum of configurations, to each of which there

[20] It is easily seen that if the symmetry of an orbitally degenerate state is Γ in any particular point group, it will contain in its energy terms linear in all those displacements with symmetry given by $[\Gamma^2]$, which is the representation spanned by the symmetrical product of Γ with itself. This will always contain the identity representation, and therefore a totally symmetric displacement; however, the corresponding term in the energy vanishes since we suppose the system to have equilibrated with respect to such displacements. It is not obvious that to each electronically degenerate species Γ, there actually exists at least one non-totally symmetric displacement of the molecule or complex whose species is contained in $[\Gamma^2]$. Nevertheless, Jahn and Teller show this to be the case for all possible realizations of all possible point groups, unless all the atom are colinear. The theorem is extended by Jahn to cover spin-orbit coupling and the two-valued representation theory appropriate to systems of odd spin. It is only the Kramers doublets, of course, that cannot be split by such ligand displacements.

corresponds a single value of χ, all with much the same energy. We may regard the ligands as undergoing a but feebly hindered "internal rotation." What is curious is not, of course, that there is a number of different configurations of the same minimum energy—clearly there are three equivalent tetragonal distortions of an octahedron—but that these should interconvert so readily. The effect has been adduced to account for certain paramagnetic relaxation times as well as for the isotropic g-factors found for copper fluosilicate (19, 21).

[Jahn & Teller (50), Jahn (51). Magnetic applications by Van Vleck (103, 104, 105) and by Abragam & Pryce (1). Hydrocarbons by Liehr & Moffitt (66).]

Optical rotatory dispersion.—One of the methods that have been employed most usefully in studying the inorganic chemistry of complexes is that of optical rotation. In many cases, particularly polydentate ligands such as ethylene diamine are sufficiently firmly attached to the central ion that they are displaced only slowly in solutions of their complexes. Different optical isomers may therefore be separated and often racemize only rather slowly. Their existence offers an attractive method of assigning certain electronic transitions.

The crystal field for a dihedral complex ion like d-$[Co(en)_3]^{+++}$ may be written in the form $(\mathcal{V}_R+\mathcal{V}_O+\mathcal{V}_D)$, where $\mathcal{V}_D$ is a small hemihedral potential. On reflection or inversion, the field becomes $(\mathcal{V}_R+\mathcal{V}_O-\mathcal{V}_D)$, which refers to the l-enantiomorph. Let us assume that the fluctuating part of $\mathcal{V}_D$, due to the vibrations, may be ignored in assessing rotational propensities; this seems reasonable, since it can affect these properties only as a result of electrical or mechanical anharmonicities. $\mathcal{V}_D$ therefore represents the static perturbation on the octahedral field for the d-isomer. Its most important function in the present context is to add to the state representative ϕ_g, of even parity, small admixtures from higher states ϕ_u, which are odd and correspond to one-electron excitations like $(3d)^{-1}(4p)$. As a result, there is a non-vanishing electric dipole moment $\boldsymbol{R}_{NV}$ associated with, for example, the transition $N \rightarrow V$ even for the static, non-vibrating complex. However, this is small—of order v say—, since it arises entirely from the hemihedral perturbation. By contrast, the magnetic dipole moment $\beta \boldsymbol{L}_{NV} = \beta(\boldsymbol{L}_{VN})^*$ for the same transition depends almost entirely on the octahedral part of the field alone; according to the selection rules for magnetic dipole radiation fields, it is of order β, or much smaller, say $\iota\beta$.

Now the rotational strength of the transition $N \rightarrow V$ is proportional to the imaginary part of the quantity $\boldsymbol{R}_{NV} \cdot \boldsymbol{L}_{VN}$ (27). It refers to the optical activity of assemblies of randomly oriented molecules—say, in solution. Being a pseudo-scalar, it remains invariant under rotations but changes sign on inversion: it depends for its value on the specific d- or l-juxtaposition of the hemihedral and holohedral crystal fields. We see immediately that $\boldsymbol{R}_{NV} \cdot \boldsymbol{L}_{VN}$ is either of order βv or of the lower order $\beta\iota v$. For the two transitions ${}^1A_{1g} \rightarrow {}^1T_{1g}$ (magnetically allowed) and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ (magnetically forbidden)

of $[Co(en)_3]^{+++}$, it will be βv in the former case and only $\beta v v$ in the latter. The one should therefore show appreciably stronger optical rotatory powers than the other. This difference offers a ready method for distinguishing between the two transitions, and others like them. It seems difficult, in fact, to find any other experimental evidence which has as direct a bearing on such assignments[21] [Moffitt (71)].

Rare earths.—Many of the historical developments in crystal field theory are due to studies of the rare earths. However, from a chemical point of view, they are less interesting than the transition metals: their properties are a more or less continuous reflection of the lanthanide contraction, with the anticipated singularities at or near the xenon structure, the half-completed and the completed $4f$ shell. The $4f$ electrons are shielded from their ligands by the completed $5s$ and $5p$ shells, so that the crystal splittings of given ionic L, S, J terms are only about 100 cm^{-1}. Accordingly the coarser features of their generally rather sharp electronic spectra are characteristic more of the free ions than of their environment. Broader systems are observed, but these are not well characterized and probably arise from transitions of $4f$ electrons to $5d$ or other states. The crystal field, which generally has rather low symmetry (C_{3h} or even C_{3v}), is of much less importance than spin-orbit coupling, since the multiplet separations are around 1000 cm^{-1}.

Spectral studies of their salts in the infra-red, visible and ultra-violet are of interest since they yield, effectively, the atomic line spectra of the ions in a specific oxidation state at concentrations equivalent to enormous path lengths in the vapour phase. Their paramagnetic resonances are also important in physics, since the associated hyperfine structures enable one to determine nuclear spins and moments. Chemically, perhaps, the main interest of these studies would lie in getting information about local site symmetries in crystals.

[Becquerel (13), Bethe (16), Penney & Schlapp (82), Kynch (61), Spedding (90), Penney & Kynch (83), Giesekus (35, 36), Hellwege & Hellwege (45), Bleaney & Stevens (22), Satten (85), Judd (58).]

Discussion and Conclusion

Before discussing the relation of crystal field theory to other methods of approaching molecular problems, we might mention that several attempts have been made to calculate the octahedral splitting factor. On the basis of assumed models for the ligands, $\mathcal{V}_O$ is explicitly constructed and the necessary quadratures are performed to obtain Dq. If each ligand is replaced by an appropriately situated point dipole, Dq may generally be fitted using reason-

[21] One might expect the hemihedral fields in the tris-ethylene diamine complex of Co^{+++} to give an estimate of the probable static distortions of the cobaltic hexammine, which have been postulated as a possible source of the intensity of band systems in the latter complex. The optical rotatory dispersion data enable one to estimate $|R_{NV}(\text{static})|^2$ for the dihedral complex (71). It turns out be to too small by a factor of fifty or so to account for the observed oscillator strengths in the hexammine.

able values of the parameters [Ilse & Hartmann (48), Bjerrum, Ballhausen & Jørgensen (17)]. However, if it is acknowledged that the electrons of the ligands are continuously distributed in space, these will overlap the electronic densities due to the central cation and orthogonality problems arise [Kleiner (59)]. Indeed, each successive refinement of such models appears to raise more questions than it answers. At present, we feel that any successes achieved by means of one model are no more encouraging than the failures of another are disheartening.

The two approaches most commonly applied to chemical problems of electronic structure are those of electron-pairing and of molecular orbitals. Both are, at first glance, very different from crystal field theory: in dealing with particular systems, even concerning transition-metal complexes, one or other of them is often used in preference to it; the metal carbonyls [Pauling (81)] and the recently developed bis-cyclopentadienyl compounds [Dunitz & Orgel (30, 31), Moffitt (69)] are examples that spring to mind. But in some ways, all three methods are remarkably similar, as was first pointed out by Van Vleck (100, 101). In the conventional valence theories, the e_g orbitals of the central cation have a tendency to accept electrons from the ligands, acting as donors—in Pauling's theory, it is these d orbitals that are used in forming his d^2sp^3 octahedral hybrids and also his square planar dsp^2 orbitals. When the tendency is strong (covalent complexes), the ground state of the ion must leave the relevant e_g orbitals vacant for bond formation. It is easy to see that this corresponds, so far as the cationic electrons are concerned, to the strong field limit of the theory we have been describing. Alternatively, when the tendency is weak (ionic complexes), the correlative interactions between the electrons overwhelm it and the electron assignments are made first according to the Hund principle of maximum multiplicity; this is equivalent to the limit of weak crystal fields [see also, Orgel (73, 76)].

The comparison of the different methods suggests certain modifications in crystal field theory. Thus, when e_g orbitals are regarded as occupied in excited states, these should be viewed as the antibonding counterparts of bonding orbitals already filled by electrons originally on the ligands. In so far as the latter electrons may be considered to migrate onto the central cation, so may electrons in the former be regarded as in part migrating to the ligands. Owen (79) has adopted this picture to rationalize the fact that spin-orbit coupling constants for free ions are rather larger than the values they apparently assume in crystal fields. It is also formally possible for the t_{2g} orbitals to participate in some double-bonding [Pauling (81)]. Stevens (92) has attributed the chlorine hyperfine structure observed in the paramagnetic resonance spectrum of the $[IrCl_6]^{=}$, $(d^5, {}^2T_{2g})$ complex to just such an effect. More strikingly, perhaps, it is well known that complexes absorb very strongly at shorter wavelengths in the ultraviolet, occasionally obscuring the relatively weak bands due to transitions within the d shell, whose properties we have described [see a review by Orgel (74), for example]. Neither the free ions nor the ligands separately show strong absorptions in this region, so that

the concomitant transitions must arise from their special relation to each other in complexes. These so-called charge-transfer spectra indicate very clearly that ligands are not content with the passive roles ascribed to them by crystal field theory. It is remarkable, however, that the presence of the excited states of charge-transfer bands do not exert a greater influence on the lower frequency behaviour of transition-metal complexes. Indeed, the extraordinary success of crystal field theory suggests that their associated motions are separable, to high approximation, from those motions primarily responsible for the magnetic and optical behaviour of the complexes with which it deals.

It will be a long time before a method is developed to surpass in simplicity, elegance and power that of crystal field theory. Within its extensive domain, it has provided at very least a deep qualitative insight into the behaviour of a many-electron system. No other molecular theory, to our knowledge, has provided so many useful numbers which are so nearly correct. And none has a better immediate prospect of extending its chemical applications.

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ION EXCHANGE[1]

By Henry C. Thomas and Galen R. Frysinger

Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut

The past two years have seen no lessening of interest either in the fundamental aspects or in the applications of the ion exchange process. If a more widespread realization of the theoretical complications of the field has perhaps contributed a larger measure of reticence in the treatment of results, it certainly has not had the effect of dampening the ardor to obtain these results.

Nearly every paper on the subject of ion exchange has in it features of interest to: (*a*) the polymer chemist, or silicate chemist, interested in the properties of the materials of his specialty; (*b*) the physical chemist looking for new leads into the structure of matter in general (and anxious to see physicochemical processes properly handled); (*c*) the analytical chemist seeking neat separations to save himself work; and (*d*) every practical chemist searching for means to expedite some reaction or process. As a consequence any separation of the two or three hundred papers which have appeared during the past two years into categories for review purposes must be highly arbitrary and left to the taste of the reviewer. It is quite possible that we have considered more than one paper from a point of view entirely foreign to the author's principal intentions in the work. However this may be, we have divided the subject into sections, and if the placement of research reports is arbitrary, the selection of individual papers for illustration and comment can scarcely be less so. It is indeed fortunate for a reviewer that those who did the work have no recourse in this matter, else a review such as this would never be written.

Equilibria in the Ion Exchange Process

A system involving the equilibrium between an exchanger of fixed capacity and a solution of two salts with a common ion in a simple solvent is evidently one of four components. The study of these equilibria requires in each case much experimental work to specify completely the state of the exchanger phase. If the exchanger is merely to be used as a tool in a separation, it may be quite sufficient to produce a limited number of selectivity coefficients. But if the object of the investigation is the nature of the exchanger itself, it will generally be necessary to study also the distribution of the nonexchange ion as well as that of the solvent.

Selectivity coefficients are expressed either quite simply as the stoichiometric equilibrium quotient for the exchange reaction:

$$RX + Y \rightleftharpoons RY + X$$

thus

$$K_X^Y = (RY)[X]/(RX)[Y],$$

[1] The literature survey for this review was concluded in December, 1955.

or with the inclusion of the solution phase activity coefficients, in which case the above expression is mutiplied by the determinate ratio γ_X/γ_Y. The definitions are modified conventionally to take care of multivalent ions if these are involved. The parentheses indicate composition units for the exchanger phase suitable to the particular investigation. Frequently these are given as moles of ion per kilogram of imbibed solvent, but they may be expressed as equivalents of ion per equivalent of exchange capacity.

The determination of the composition of the exchanger is generally best done by more or less direct analysis. A considerable difficulty is here encountered in ensuring that no changes in composition occur on separating the exchanger from the solution phase. In principle this difficulty can be avoided by never doing a separation but by relying on differences to give the composition of the exchanger. Such a procedure is, however, subject to serious drawbacks: it is impossible to get a complete material balance in a single experiment, and all analytical errors are magnified in the calculation of the selectivity coefficients. Unless the analysis of the exchanger phase is prohibitively difficult, which generally it is not for resinous exchangers, complete analyses of both phases should be made, as in most work they are.

Distribution of the Solvent

The very important point of the solvent uptake of the exchanger phase is generally best studied by an isopiestic experiment using a well characterized exchanger composition. Significant studies of this nature have recently appeared. Soldano & Larson (1) have reported a comprehensive investigation of the equilibrium water uptake of anion and cation exchangers as a function of water activity. These authors express their results in terms of a practical osmotic coefficient, ϕ, related to the water activity, a_w, the activity of the water vapor, and m, the stoichiometric molality of the resin salt (calculated per kg. H_2O) through the equation

$$-\log a_w = 0.00782\phi m.$$

The region of validity of this (somewhat simplified) expression is shown to be above $2m$ for both the anion and cation exchangers investigated. The anion exchangers studied were lightly cross-linked (0.5 per cent divinylbenzene): Dowex 2, a dimethylethanol quaternary ammonium ion resin, and Dowex 1, a trimethyl quaternary ammonium resin. It was found both for the anion exchangers and for the cation exchanger studied (Dowex 50, a polystyrene sulfonate) that the osmotic coefficients could be represented by the equation given by Scatchard & Breckenridge (2)

$$\phi - \phi_0 = am(1 + bm).$$

In the case of the anion exchangers the range over which this expression fits the data is $2 < m < 30$; for the cation exchanger, $2 < m < 15$. Tables I and II, adapted from Soldano & Larson, summarize the results of their work. These osmotic coefficients enable a calculation of selectivity coefficients; this cal-

TABLE I

PARAMETERS FOR THE OSMOTIC COEFFICIENT, ANION EXCHANGES*

$\phi - \phi_0 = am/(1+bm)$

Salt Form	Dowex 1 $\phi_0=0$		Dowex 2	
	a	b	a	b
ClO_4^-	0.001	−0.035	0.0035	−0.013
I^-	—	—	.0147	−0.010
Br^-	.051	.0	.0635	+0.02
Cl^-	.135	+0.03	.153	.05
OH^-	.426	.07	—	—
F^-	.578	.12	.54	.10

* From Soldano & Larson (1).

culation is discussed in some detail by Soldano & Chesnut (3), who have measured selectivities as functions of resin composition and structure and compare the experimental results with values calculated from the osmotic coefficients. These methods are applied to cation exchangers by Soldano *et al.* (4). Soldano and his co-workers are careful to point out that the meth-

TABLE II

PARAMETERS FOR THE OSMOTIC COEFFICIENT, CATION EXCHANGER*

$\phi - \phi_0 = am/(1+bm)$

Salt Form	Dowex 50		
	a	b	ϕ_0
H	0.17	−0.02	0.40
Li	.157	+0.02	.40
Na	.065	−0.01	.39
NH_4	.0307	−0.015	.47
K	.0098	−0.050	.40
Cs	.0068	−0.055	.41
Ag	.007	−0.055	.25
NMe_4	.3255	+0.09	.00
NEt_4	.467	+0.10	−0.22
La	.098	−0.026	−0.32
Zn	.208	−0.021	−0.28
Cu	.166	−0.022	−0.22

* From Soldano & Larson (1).

ods proposed involve an assumption as to the behavior of the osmotic coefficient at high dilution, information not now available, and belonging to a region inaccessible with true resins. An approach to this problem has been made by Bonner *et al.* (5) who have determined osmotic coefficients for the *p*-toluene and *p*-ethylbenzene sulfonic acids. These authors show that the correct sequence of selectivities—Li, H, Na, K on a 4 per cent DVB (divinylbenzene) cation exchanger—is obtained from the appropriate ratio of activity coefficients,—their own data on the acids place hydrogen in the proper position. Studies of a related nature have been reported by Bonner & Payne (6), who have measured equilibria involving Li, H, Na, NH_4, K, and Ag on Dowex 50 (8 per cent DVB) at constant ionic strength.

The solvent influence is accentuated (and undoubtedly immensely complicated) by the addition of other components. Quite specific effects have been demonstrated in exploratory work by Bonner & Moorefield (7) in a study of the Ag—H system on Dowex 50 in EtOH-water and dioxane-water solutions. The composition and amount of the imbibed solvent was determined for the pure Ag and H forms of the resin. The selectivity of the resin for silver was slightly increased by alcohol up to 25 per cent. At 75 per cent a very large increase was found for the resins rich in silver, while the effect remained moderate for low silver content. Kakihana & Sekiguchi (8) find a similar effect in Na—H exchange from water solutions of acetone; the selectivity for sodium increases with acetone content. These workers find a linear relation between logarithm of an equilibrium quotient and the reciprocal of the dielectric constant of the solvent. Gregor *et al.* (9) have made quite a comprehensive study of the distribution of alcohols and dioxane between water solutions and a polystyrene sulfonic acid in the ammonium, quaternary ammonium, and silver forms. The cation in the resin strongly affects the selectivity of the absorption. A similar study was made for an anion exchanger in ethyl alcohol-water mixtures. Exchanges of Ba—Na in alcohol-walter solutions and Na—NH_4 in acetone-water solutions have been studied by Materova *et al.* (10). Increase in the organic content of the solvent enchances the selectivity for sodium in both cases.

In much of the work that has been done on the role of the solvent in the ion exchange equilibrium, the vague concept of ionic hydration has been used in attempts to account for selectivity. It is probably true that these explanations have been possible only because of the vagueness of the concept. In the past year the complete work of Glueckauf & Kitt (11) on this subject has been published. Their paper is important not only for the experimental results which it makes available but especially for its clarifying discussion and amplification of the concept of ionic hydration. Glueckauf and Kitt have made isopiestic measurements, particularly in the region of low water activity on lightly cross-linked (0.5 per cent DVB) polystyrene sulfonates. Nine salts of singly charged ions and six salts of doubly charged ions have been studied at different temperatures, with the majority of the data at $a_w < 0.3$. The detailed information thus obtained on

the water isotherms has made possible the calculation not only of the free energies but also of the enthalpies and entropies of the adsorption process. For the interesting arguments, based on the thermodynamic data, by which the authors arrive at a model which accounts in detail for these results, the original paper should be consulted. It will be useful to summarize here the principal conclusions of this work. From the shape of the isotherms at small a_w it is deduced (by a method of successive exclusions) that the first water molecule adsorbed by a resin salt causes a dissociation into two ions, more or less distinct, and further that this water molecule in the case of a resin salt (not a resin acid) is bound to the sulfonate group. Successively added water molecules become associated with the cations. Using this model the authors deduce quite simply a formula for the adsorption isotherm which involves a series of equilibrium constants approaching unity for high ratios $R = H_2O/\text{ion}$ (moles). Their formula is, for $K_4, K_5 \cdots = 1$,

$$R = \left[1 + \frac{K_2 a_w}{\epsilon}\left(1 - K_3 + \frac{K_3}{(1 - a_w)^2}\right)\right]\sqrt{\frac{K_1 a_w \epsilon}{1 + K_1 a_w \epsilon}}$$

$$\epsilon = 1 + K_2 a_w + \frac{K_2 K_3 a_w^2}{1 - a_w}$$

TABLE III

EQUILIBRIUM CONSTANTS FOR WATER ADSORPTION*

Resin Form	Salts of polystyrene sulfonate (0.5 per cent DVB)					
	0°			25°		
	K_1	K_2	K_3	K_1	K_2	K_3
H	325	33	4.5	93	16	3.8
Li	185.5	7.3	3.6	65.8	4.1	2.3
Na	149	5.7	3.0	57.0	3.5	2.0
K	77	3.5	1.2	33.0	2.5	1
Cs	56.8	3.2	1	21.5	2.9	1
Ag	45.0	2.41	1	15.0	1.38	1
NH_4	31.5	2.46	1.3	15.0	2.1	1.1

* From Glueckauf & Kitt (11).

Table III from Glueckauf and Kitt gives values for the constants which adequately reproduce the data at all except high water activities ($a_w >$ ca. 0.7). For those ions which according to Table III are satisfactorily cared for with K_3 also unity the above formula for the isotherm is considerably simplified. For salts of Li and H larger numbers of constants are necessary. Indeed, with the resin acid another adsorption scheme must be predicated, which, however, leads to a similar equation for the isotherm.

On the basis of this work it now becomes possible to give an operational

definition to the term "ionic hydration at infinite dilution." This the authors do as follows: The "free swelling water" of the resin is defined as that water which is taken up with zero free energy change ($K=1$); this is given by $R_s=a_w/(1-a_w)$. Introducing the (extra thermodynamic) conclusion that the first water is attracted to the sulfonate group, the cationic hydration is then given by

$$R_h^c = R_{obs.} - 1 - R_s$$

(One subtracts 2 if two sulfonate groups are involved, as with a divalent ion.) In order to obtain results for $a_w \to 1$ a somewhat modified approach is necessary. The K_n for high R reach values below unity (this is ascribed to ionic interaction), and the formula is therefore modified to read

$$R_h^c = R_{obs.} - 1 - K_n a_w/(1 - K_n a_w).$$

The value of K_n for each ion is determined by the condition that the hydration number should change little near infinite dilution. (These K_n values are near unity.) This permits the determination of the limit of R_h^c for $a_w=1$, which is defined as the cationic hydration number. Glueckauf & Kitt report values of K_n for all ions studied except NH_4, for which the results are uncertain. Thus for Li, Na, Cs they find for hydration numbers 3.3, 1.6, 0.6; for Ca, Sr, Ba; 5.2, 4.7, 2.0 (all at 25°). The authors are careful to point out that these hydration numbers are, in effect, a particular kind of average. They give an enlightening set of curves which show the contribution to total water adsorption at various water activities of the various adsorption steps. Thus there is no case for the idea of a definite shell of water molecules about an ion at a given water activity.

Nearly every investigations involving an ion exchanger for whatever purpose may in some part be reduced to a study of the distribution of ions between exchanger and solution. In most work no attempt is made to specify exactly the equilibrium composition of the exchanger; such a specification would, as we have mentioned, be superfluous in the development of a separation procedure for analytical purposes. In spite of the fact that much significant data is likely to be found in the general literature of the applications of ion exchange, we shall not attempt the forbidding task of unearthing this material, but will confine our considerations to papers primarily intended as "theoretical" equilibrium studies. A connected discussion of even this smaller group is difficult: there are nearly as many points of view as authors. We shall simply take the easy if inessential path through cation exchangers via ions of increasing complexity, past anion exchangers, and finally to the absorption of nonexchange ions.

Cation Exchanges

The fundamental predicate of the reversibility of the ion exchange process has been invesigated by Saldadze (12), who finds complete reversibility for Ba—Mg, K—Ba, and Zn—Cd on a sulfophenolic resin. Saldadze (13) has

also investigated the dependence of the composition of the resin on the dilution of the equilibrating solution and finds no effect when the charges of the pair are alike (but *v. infra*) and a change in composition for ions of unequal charges. A similar result with Amberlite IR-120 has been obtained by Reiner, Schulz & Tezak (14). A careful experimental study of this point has been reported by Wilson *et al.* (15), who studied the Ag—Na exchange on Dowex 50 at ionic strengths from 0.01 *M* to 1 *M* at 25°. In this work the resin was washed with water before analysis and as a consequence it is difficult to see how the presence of nonexchange electrolyte originally in the resin affects the results of their calculations. Equilibrium "constants" calculated essentially on the supposition of a two component system vary from 6.63 at 0.01 *M* to 7 6 at 0.3 *M*, with a value of 6.54 given by extrapolation to infinite dilution. (The composition of the resin is here expressed as equivalent fraction.) This unsatisfactory behavior of a thermodynamic constant will undoubtedly resolve itself when the system is treated completely.

Bonner (16) gives relative stoichiometric selectivities on Dowex 50 with various degrees of cross-linking for the ions Li^+, H^+, Na^+, NH_4^+, K^+, and Ag^+. These selectivities increase in the order given, and except for a small anomaly with hydrogen, increase with increasing stiffness of the resin. Bonner (17) has also studied equilibria involving Rb^+, Cs^+, Tl^+, and H^+ on Dowex 50 and has determined the maximum water uptake of the resins in the various forms.

Reichenberg & McCauley (18) have studied the following pairs on polystyrene sulfonates of four degrees of cross-linking (5.5, 10, 15, 25 per cent DVB): H—Li, Na—H, K—H, Na—Li, K—Li, K—Na. Inversions in affinity occur where hydrogen is involved for the stiffer resins. Generally speaking, however, Bonner, Reichenberg & McCauley agree as to the order of selectivity.

Other investigations involving equilibria with the hydrogen form of cation exchangers are those of Yamabe (19) and Högfeldt (20). The former reports a rather comprehensive study of the Na—H exchange on Amberlite IR-120. Högfeldt's work is concerned with the distribution of silver between the resin Wofatit KS and solutions at ionic strength 0.1 containing 10^{-2} to 10^{-7} moles of silver per liter. The coefficient K_H^{Ag} has a constant value 0.26 for the mole fraction of silver in the resin between 7×10^{-6} and 4×10^{-3}.

A comprehensive discussion of the thermodynamics of Na—H and Ba—H exchanges on Dowex 50 of various cross-linking has recently been published by Duncan (21). The equilibria have been determined at different temperatures and thus the calculation of the enthalpies and entropies of the reactions has been made possible. Duncan interprets the results as indication that for the Na—H resins the ionic condition in the resin phase is similar to that in the aqueous phase at like concentrations; ionic interactions are considered to be small. In the Ba—H resins the divalent ion shows strong interactions with the anionic groups of the resin.

In a study of Mg—K exchanges on Dowex 50 (10 per cent DVB) Gregor

et al. (22) show that if the selectivity coefficient (in molal units) is defined to include the solution phase activity coefficients quite constant values for the K_K^{Mg} over a wide range of resin compositions and from N = 0.001 to 1.0 for the external solution. Their average value is $K_K^{Mg} = 0.14 \pm 0.02$.

Diamond (23) has studied with the tracer elution technique the equilibria on Dowex 50 of concentrated solutions of hydrochloric acid of the ions Be^{++}, Ca^{++}, Ba^{++}, Ra^{++}, Na^{+} Rb^{+}, and Cs^{+}. The distribution ratios are given as functions of acid concentration. Reversals in the order of elution of the alkaline earths are found as the acid concentration is increased to 12 *M*. Reversals for the alkalis occur at lower acid concentrations. Evidently the effects are complicated and a knowledge of all of the factors entering into the exchange equilibria would be necessary for an adequate discussion. A qualitative accounting is given by the author in terms of ionic hydration.

Strocchi (24) emphasizes on the basis of studies of Ba—H and Ba—Na exchanges on Amberlite IR-120 and Amberlite IR-50 that the complete characterization of an exchange reaction requires the knowledge of the selectivity coefficient for an ion pair as a function of the composition of the resin phase.

Davydov & Levitskiĭ (25) have studied many-ion exchanges in which, for example, a resin containing NH_4, Ca, and Fe was equilibrated with a solution of a fourth cation. Coefficients for an equilibrium expression are given.

Other many-ion exchanges have been the subject of investigation by Wiklander & Nilsson (26). These workers add hydrochloric acid to a suspension of Amberlite IR-100 which contains already two metal ions (e.g. Li and Na). The acid is added in successive small amounts. Between additions the solution is completely removed for analysis. These workers find different cumulative ion releases if the acid is added in larger portions and state "that a desorption taking place successively and in small quantities, in comparison with a larger desorption, tends to conserve the firmly adsorbed ions at the expense of the weakly adsorbed ions." The authors are discussing the behavior of a five component system in which the composition is changed by two paths. The present writers must confess that the significance of these results is unclear to them. It is, however, certainly true that the systems studied are incompletely characterized.

Anion Exchanges

If we exclude from consideration at this point a large number of important papers involving anion exchange studies, which more properly may be classed as studies on the nature of ions, there remain only a few investigations dealing with equilibrium proper on anion exchangers.

Gottlieb & Gregor (27) base their presentation on the "reduced mean activity coefficient"

$$\gamma_{\pm}^{r}/\gamma_{\pm} = m/(m_{+}^{r}m_{-}^{r})^{1/2}$$

resulting from equating the activity of the diffusible electrolyte in the resin

phase (superscript r) to that in the solution phase. Knowledge of the resin exchange capacity, content of nonexchange electrolyte and water content enable the calculation of the ratio of activity coefficients. The anion exchange resin used was Dowex 2 (8 per cent DVB), and equilibria were measured for K acetate, KCl, KSCN, KI, NaOH, HCl, and K trichloroacetate. At high external concentration the ratio approaches unity in all cases and decreases very sharply with decrease in concentration. The results are discussed in terms of ion pair formation between the fixed group and the exchange ion.

In an extensive work Gregor *et al.* (28) have measured anion selectivity coefficients on a series of resins (Dowex 2) of different degrees of cross-linking. The effects of temperature and concentration are both found to be small. The ions studied divide into two groups according to the behavior of the selectivity coefficient as the resin composition changes. Coefficients for pairs from within a group show little dependence on composition; coefficients for pairs made up of one ion from each group show a marked dependence on composition. The groups are: (*a*) halide, acetate, iodate, nitrate; (*b*) thiocyanate, perchlorate, di- and trichloroacetate, trifluoroacetate, toluenesulfonate, naphthalene sulfonate. These results are interpreted to mean either random or clustered association of the ions with the matrix of the exchanger. For the details of this discussion the reader is referred to the original paper.

The complicated problem of the sulfate-bisulfate equilibrium on a resinous exchanger is the subject of a paper by Anderson *et al.* (29). Using data from the literature on the ionic composition of sulfuric acid in solution, the authors are able to calculate from their equilibrium measurements values for $K_{HSO_4^-}^{SO_4^=}$ on Dowex 1 (8 per cent DVB). An interesting possibility arises from this work: the resin in the sulfate form can be used to remove sulfuric acid, or indeed any strong acid, from solution. In the process it is converted to the bisulfate form. The resin is regenerated simply by passing water over it. The most serious limitations of the process as a commercial possibility are that the acid removed from the resin must be more dilute than that originally absorbed and that very dilute acids cannot be picked up efficiently. The process may with advantage be used for the removal of strong acids from solutions of nonelectrolytes.

The Nonexchange Ion and Neutral Molecules

An important contribution to the literature of equilibria on ion exchangers is the rather extensive work on the nonexchange ion by Whitcombe *et al.* (30). In addition to distribution data for Na—K on Dowex 50 (for solution concentrations from 0.0134 *N* to 2.7 *N* in chloride solutions) they give the following equations for the relation between the molalities of absorbed chloride ion, m^r, and chloride in the exterior solution, for unmixed resins,

$$\text{Na resin, } m^r = 0.137\, m^{1.52}$$

$$\text{K resin, } m^r = 0.165\, m^{1.52}$$

These results are based on determinations for NaCl $1.46 < m < 6$, and for KCl $0.88 < m < 4.47$. The authors employ thermodynamic considerations which enable them to give values of m^r down to very low concentrations. They find for $m = 0.0001$, $m^r = 4.69 \times 10^{-9}$ in the sodium resin and $m^r = 5.79 \times 10^{-9}$ in the potassium resin. Whitcombe, Banchero & White have interesting comments to make on the difficulties in the interpretation of rate-of-transfer measurements when the anion content of the exchanger changes with the cation content.

Krishnaswamy (31) has reported the chloride uptake of phenosulfonic acid—formaldehyde membranes in solutions of hydrochloric acid, sodium chloride, and barium chloride, that for the barium solutions being the greatest. Below 1 *N* he finds a constant ratio of concentrations resin/solution.

The study of the absorption by ion exchangers of neutral molecules other than water, acetone, and simple alcohols seems to have received scant attention recently. Rückert & Samuelson (32) have measured the uptake of sucrose and glucose by both cation and anion exchangers from alcohol-water solutions. On the basis of experiments with desulfonated resins they conclude that the polymer network is of little importance in the process.

Kinetics in Ion Exchange

In principle, but not generally in practice, if the rate law governing the interchange between exchanger and solution is known, satisfactory calculations of the rates of exchange in both batch and flowing systems can be made. It has now long been demonstrated that the kinetic behavior of most exchange processes is determined by some diffusional mechanism. Depending on the conditions of the experiment and the relative magnitudes of diffusion coefficients, the rate limiting transfer is either diffusion in the solution phase or diffusion within the exchanger itself. Application of this knowledge is always made unsure by hydrodynamic considerations. In batch exchanges there is uncertainty as to the thickness of unstirrred films; in flowing systems a simple velocity profile for the fluid must be assumed. In all but the most highly idealized cases geometrical difficulties with shapes of particles and films complicate the calculations.

The most satisfying demonstrations of the diffusion mechanism have been made possible by the use of isotopic tracers. Here the considerations are enormously simplified; only self-diffusion need be in question and the intricate considerations necessary for polycomponent diffusion need not obscure conclusions concerning the mechanism of transfer. Even for this simpler case complete studies must be concerned not only with self-diffusion of the exchange ion but with that of the solvent and the nonexchange ion as well, and, in general, these for a variety of equilibrium compositions.

In the period which concerns us, only one study approaching this comprehension has appeared. Tetenbaum & Gregor (33) have studied self-diffusion in polystyrene sulfonic acid of the potassium and chloride ions and water. Using both flowing systems, in the shallow bed technique, and batch

experiments, these workers have obtained significant results, which are generally in agreement with the ideas of particle and film diffusion. In their shallow bed experiments, through the concentration range 0.0001 *M* to 0.1 *M*, excellent agreement was obtained with curves calculated for a constant film thickness and a single diffusion coefficient. The fact that it was necessary to assign to potassium a self-diffusion coefficient somewhat different from the value reported for free solution is not very disturbing in view of recent discussions as to the accuracy of our knowledge of these quantities. Tetenbaum & Gregor find a concentration-dependent particle diffusion coefficient for chloride, the nonexchange ion, near 8×10^{-6} cm.^{2}/sec. Experiments on the rate of exchange of deuterated water give the interesting result that the exchange of water within the particle is nearly as rapid as in free solution. These results were obtained with a moderately stiff resin, 12 per cent DVB.

Sugai & Furuichi (34) report a study on the self-diffusion in Dowex 50 of calcium in which measurements have been made at different temperatures. In 1 *M* solutions particle diffusion is found to be the controlling rate (film diffusion sets in below 0.5 *M*), and values as follows are reported for the self-diffusion coefficient, $D\times10^8$: 1°, 0.84; 9.8°, 1.3; 20.2°, 3.7; 30.7°, 4.0, with an activation energy of 1.4 kcal./mole.

In work with ion exchange resins the plaguy geometrical considerations of diffusion experiments can, so to speak, be pushed to the edges if use is made of molded discs of the material. A preliminary report of work of this character by Holm (35) has appeared. Holm has measured self-diffusion of Na^+, Ca^{++}, and Sm^{+++} in such discs. The coefficient is found to decrease rapidly with increase in the charge of the ion, in conformity with earlier work of this character by Boyd & Soldano.

In early 1954 the last of the important series of papers by Boyd & Soldano appeared; Boyd *et al.* (36) report a study of self-diffusion in desulfonated cation exchange resins. Self-diffusion coefficients for Na^+, Ag^+, Zn^{++}, Y^{+++}, and La^{+++} first increase as cross-links in the exchanger are broken; but with further decomposition of the exchanger and consequent destruction of exchange sites, the coefficients decrease and activation energies take on large values.

Another type of influence on the motion of an ion through the matrix of an exchanger is made clear by the work of Conway *et al.* (37). They have measured rates in the Na—H exchange on the carboxylic acid resin Amberlite IRC-50. Here self-diffusion coefficients are not in question, but the kinetic data are interpreted in terms of an effective diffusion coefficient for sodium and hydrogen with a value of 4×10^{-9} cm.^{2}/sec. This value, a thousand-fold lower than that for a sulfonic acid exchanger, reflects the low concentration of hydrogen ion within the weak acid resin.

Ions more complicated in structure than those of the light metals have received attention. Kawabe *et al.* (38) have studied the rate of absorption of nicotine from solution into both sulfonic acid and carboxylic acid ex-

changers. In the neighborhood of 0.2 mole/l. diffusion within the absorbing particle is found to be the important point. An interesting specific effect has been found by Nomitsu & Hironaka (39) in the rate of exchange of molybdate ions with the anion exchanger Amberlite IRA-410. The effective diffusion constant decreases with the pH of the solution and becomes about constant below pH 3.8. This appears to be due to the larger size of the molybdate ion in the more acid solution.

The fact that the kinetics of the ion exchange process is of great interest to the soil scientist, who must concern himself with the mechanism by which plants pick up their nutriment, is evidenced by the work of Krishnamoorthy & Desai (40). These workers have been studying the complicated processes by which ions are passed from exchanger to exchanger all suspended in the same medium. Diffusional mechanisms are found to be significant. It is, however, easy to see why interpretations of work of this character must be made with care. The boundary value problems for the diffusion equations would appear to be somewhat involved.

Let us now turn to a consideration of the developments in the field concerned with the interaction of solid exchangers and fluids in bulk motion, i.e., chromatography and the performance of ion exchange columns. In any practical ion exchange application the advantages to be gained from a flow rather than a batch process are too well known to need comment. The extraordinary fertility of the various modifications of chromatographic method has produced significant advances in nearly every branch of chemistry during the past decade. We shall not attempt to summarize here any of these results but shall confine our attention to developments in the mathematical treatment of the process.

As is usually the case in any scientific application of general principles, the history of the theory here can be traced far back of the current applications. The equations used by Rayleigh in the nineteenth century for a discussion of the propagation of shock fronts in his theory of sound are identical in form with those required to describe the propagation of the boundary of a zone in single solute equilibrium chromatography. Fundamentally the processes are alike: entropy is being rapidly created in the motion. But with increasing complication of the chromatographic case and the necessity to take into explicit account some, at least, of the many nonequilibrium effects, the mathematical treatment of the subject has become increasingly more involved. We appear to have reached a point of diminishing returns in this field. Qualitative clarification we have and use; quantitative descriptions are frequently so involved as to be out of practical reach. It is most fortunate, for example, that the separation of the amino acids from insulin was not dependent on a knowledge of mutual influences on their distribution coefficients! However, advances have been made in the treatment of the performance of ion exchange columns, and these advances have been put in usable form and not merely left as shapeless heaps of transcendental functions.

Vermeulen & Hiester have continued their work in adapting to various situations the solutions of the rate dependent equations for the ion exchange column based on opposing second order reactions. This approach has proved to be of considerable flexibility; the rate law in effect subsumes the cases of film diffusion and the first approximation to the solid diffusion case, as well as allows one to take account of nonlinear isotherms. Vermeulen & Hiester (41) have extended the treatment to cases of mixed feeds and partial presaturation of columns. That the approach is satisfactory is demonstrated by experimental work of Baddour *et al.* (42) on the elution of columns of Dowex 50 partly saturated with H^+ and Na^+. Data based on operation of the same columns under saturation conditions enable the prediction of the performance with partial saturation. Baddour and his co-workers give a useful summary, in the form of tables of appropriate formulas, of the regions of applicability of the various limiting forms of the theoretical equations.

Lapidus & Rosen (43) give a very informative discussion of what has been called "the constant band width approximation" to the performance of an ion exchange column. The conditions under which a front of unchanged shape moves down a column are in effect determined by the balance between the sharpening effect of chromatography, for a curved isotherm, and the smearing effect of a finite rate of adsorption. The shape of such a front may be obtained as an asymptotic solution of a complete equation for the process, or as Lapidus and Rosen show, directly from a consideration of the isotherm and the rate law. For a case of wide utility, film diffusion mechanism and Langmuir isotherm, a simple result in closed form is obtained for the shape of the front. This result is applied to data at very fast rates of flow for the exchange of sodium for hydrogen on Dowex 50 (4 per cent and 8 per cent DVB) in which only the length of the column is varied. The results are all that could be desired; the linear portion of the isotherm fails to give a "final front," and the effects of a small contribution due to solid diffusion are to be seen for very long columns of the stiffer resin. There can be no doubt that all significant effects have been accounted for in this work.

The technique of handling an ion exchange column by the method of gradient elution has been applied in a separation of carrier free "activities" by Nervik (44). A continuous variation of the pH of the eluent makes possible a considerably shortened operating time in this application. A mathematical description of the gradient elution method has been given by Freiling (45) based essentially upon plate theory and the Gaussian approximation to the shape of an elution peak. The author points out the limitations of the method, the most serious of which appears to be the necessity for the use of the Gaussian approximation for a small number of the theoretical plates.

Simpson & Wheaton (46) discuss the analysis of column behavior in the ion exclusion technique and analyze by the plate procedure a separation of ethylene glycol on Dowex 50.

Preparation and Characterization of Ion Exchangers

Insofar as the synthesis of ion exchangers is concerned, much of the emphasis during the past two years has been on the preparation of more carefully characterized materials. From the very beginnings of work in the field of ion exchange the demand most difficult to satisfy has been for an explicit statement of the character of the materials involved. So stated, of course, the demand cannot be satisfied, but the most ardent devotee of the field would agree that qualitative advances are much to be desired. Some of the best work employing the ion exchanger as a tool in chemical research has relied on the simple and effective device of using always an exchanger from a single preparation. In the long run such a course cannot be entirely satisfactory, and recent work aimed at producing a planned and reproducible result in synthesis is very welcome indeed.

Graydon and his co-workers at the University of Toronto have made an important advance in the synthesis of ion exchange resins. Thus Spinner *et al.* (47) have brought about the polymerization of esters of *p*-styrenesulfonic acid with divinylbenzene and by hydrolysis after polymerization have produced resins in which no disulfonated benzene rings are to be found. Furthermore the active sites in these resins are certainly expected to be more uniformly distributed through the matrix than for a material produced by sulfonation after polymerization. The esters were found difficult to purify, and unfortunately it was necessary to use a somewhat crude product in preparing the resins. After hydrolysis the resins were conditioned through the sodium-hydrogen cycle. Values of K_H^{Na} were determined for the resin prepared from the *n*-butyl *p*-vinylbenzene sulfonate. The equilibrium quotients showed little variation with composition for mole fraction of sodium in the resin between 0.2 and 0.8. The authors give an interesting discussion of their results in terms of a simple model which in effect supposes the resin to be made up of two classes of non-interacting sites in a definite proportion, and that each class behaves in an ideal fashion in the exchange; i.e., the resin is supposed to be completely characterized by two equilibrium constants and a parameter describing its composition. Since this model supplies the worker with three adjustable parameters, it is perhaps not so surprising that the data showing a simple behavior such as that found by the authors for their hydrolyzed sulfonates are reproduced by a suitable choice of constants. It is, however, significant that for this resin 97 per cent of the sites must be supposed to be of one class. Interest in the model increases when it is observed that earlier work of Reichenberg and of Bonner in which the equilibrium quotients show a marked dependence on composition are likewise reproducible in terms of the model, and that in these cases the major class contains 87 per cent and 62 per cent instead of nearly all the sites. This method of treating equilibria is, of course, extra-thermodynamic in character; which is no criticism, but it remains to be seen how far its implications may be accepted. In the meantime it is certainly true that the procedure is a useful method of correlating data. In essence the

method is very like that used by Glueckauf & Kitt (11) in treating the absorption of water. It is to be hoped that the method will be extended and the scope of its usefulness accurately defined.

Other well characterized exchangers have also received attention recently. Gregor *et al.* (48) have studied the properties of cross-linked polyacrylates. These acids appear to be weaker than their linear counterparts at similar salt concentrations. Howe & Kitchener (49) have studied the titration and adsorption of water in rods of polyacrylic acid cross-linked to different degrees with glycol bismethacrylate. The water adsorption of these materials is of particular interest. The first adsorbed molecules are extremely strongly held and appear to produce dissociation: the isotherm approaches the axis of water adsorbed nearly tangentially (convex up). With the partial neutralization of the acid group the isotherm flattens and eventually becomes convex down, over nearly the entire range. A complete and quantitative analysis of these results would be very desirable.

The mechanics of polymer-solution interaction have been the object of quite direct attack by Katchalsky & Zwick (50). These workers have studied the force-elongation properties of fibers of ion exchangers and have discussed the results with the aid of theory relating recoverable mechanical energy to the energy involved in mixing uni- and bivalent ions in the exchanger.

Matsuura (51) has studied the heats of wetting of a number of exchangers in different ionic forms. It is significant that the heats of wetting of partially wetted materials show that only the first few water molecules contribute markedly to the heat effect.

The study of electron exchangers (redox polymers) introduced by Cassidy and his co-workers has been continued (52). Manecke (53) has continued work with the condensation products of hydroquinone with phenols, polyhydric phenols and formaldehyde. He has used potentiometric (53) and column methods (54) in the characterization of these materials. Similar polycondensates have been studied by Soloway & Schwartz (55) and by Kropa (56). The preparation and properties of two polythiolstyrenes have been reported by Gregor, Dolar & Hoeschele (57) and by Overberger & Lebovits (58). Certainly these interesting materials are as yet far from the state of development which they deserve, in view of the many interesting and important applications to which they might be put.

Inorganic Ion Exchangers

The phenomenon of ion exchange—as is well known—was discovered a hundred years ago in connection with the behavior of soils toward fertilizers, or "manures" as they were called by Way. Probably both organic and inorganic exchangers contributed to the effects first observed. Certainly for many years after the discovery inorganic exchangers came in for the lion's share of attention. The interest in the subject on the part of the soil scientist has never abated, and he has done much work on the ion exchange behavior

of the clay minerals, the principal contributors to the effect in soils. In recent years interest in the subject has been extended by the highly practical necessity of learning what to expect in the interaction of the radioactive waste products of uranium fission with soil minerals. During the past twenty-five years the clay mineralogist has elevated the object of his study into the class of well-characterized compounds, and considerable scientific as well as practical interest has become attached to the investigation of the ion exchange properties of clay minerals. These exhibit a selectivity for cations, very marked in some cases, similar to that of a sulfonic acid exchanger. Precise studies of these effects have recently occupied one of the present writers (59, 60). The methods employed are entirely similar to those used with resinous exchangers with only modifications made necessary by the small particle size of the clay mineral. Static equilibrium studies with fine particles are troublesome because of difficulties in separation. These have been replaced by the more laborious technique of the "equilibrium column." The results are independent of the nonequilibrium effects in the column, which here is used merely as a convenient method of separating exchanger from solution.

The seat of the ion exchange effect in the montmorillonite and attapulgite minerals is well understood: a replacement of silicon by aluminum or of aluminum by a divalent metal is the counterpart in a clay of a sulfonic acid or carboxyl group in a resin. The situation in the kaolin clays is not so well understood, although recent work by Robertson *et al.* (61) produces evidence that replacements in the tetrahedral sheet of kaolin produces at least a part of the effect in this mineral.

Cation exchange behavior in a variety of other silicates has received attention recently. The very low capacity of talc (0.2–0.4 meq./100 g.) has been shown by Kingery, Halden & Kurkjian (62) to be independent of the state of subdivision of the mineral. Barrer & Raitt (63) have made an extensive study of ion exchange in ultramarine, in which diffusion coefficients as functions of temperature, and the derived functions attached to the activation process, have been determined for several exchanges involving the univalent ions.

Important investigations related to the ion exchange properties of the montmorillonites have been carried out by Barrer & MacLeod (64). When tetraalkyl ammonium ions occupy the exchange sites in a montmorillonite, the materials so formed exhibit many unusual properties and in particular show marked absorptive power for organic molecules. Barrer & MacLeod have measured adsorption isotherms in these systems for A, O_2, N_2, NH_3, alcohol, benzene, and several aliphatic hydrocarbons.

Mineral anion exchangers are not numerous. The exchange properties of apatite have long been known and have recently received attention from Weikel *et al.* (65) in connection with studies of the chemistry of bone. Surface hydroxyl groups of the clay minerals apparently act as anion exchangers, but the effects are small. Undoubtedly the anion exchanger of-

fering the most promise as a tool for the chemist is hydrous zirconium oxide, as very recently announced by Kraus & Phillips (66). Zirconium hydroxide is precipitated by ammonia from oxychloride solutions, washed, dried, and ground. The drying temperature has much influence on the properties of the substances so prepared. In acid solutions they show all the properties of weak-base anion exchangers; in basic solution they absorb cations. As anion exchangers these preparations will certainly find important uses in separations and in the study of solutions.

Separations Produced by Ion Exchange

A basic knowledge of the chromatographic technique and of the nature of ion exchangers is a prerequisite for the chemical business of making separations. Any lingering doubts on this score will be speedily dispelled by a look at the number and character of new separations made possible by the techniques of ion exchange.

The most difficult separations of all, those of isotopes, have been successfully carried out. The rare earth work has become a classic even before the work has been finished. Numerous separations of cations, anions, and of organic materials, ionic as well as neutral, are greatly facilitated by the method. The applications are so widespread that the writers feel inclined to express a fear that the method may be taken by the uninitiated as a cure-all and an excuse not to bother to learn any more inorganic chemistry. A look beyond the actual results will show quite clearly, however, that new successes have come to those who are able to use a wide knowledge of chemistry and who can twist the chromatographic technique to their own ends.

A discussion here of every separation made public during the past two years, aside from being impractical, would be nearly useless. We shall content ourselves with three examples which we think well illustrate the points just made and shall append a catalog which we hope is sufficiently complete to be of value.

A masterly application of theoretical and practical knowledge of the operation of ion exchange columns has very recently been published by Spedding *et al.* (67, 68). These workers have brought about a practical separation of N^{15} by methods similar in principle to those used in the rare earth separations. Ammonium hydroxide has been placed on a column and driven many feet forward with an eluting solution of sodium hydroxide. The reaction taking place at the head of the zone,

$$H^+(r) + NH_4OH(s) \rightleftharpoons NH_4^+(r) + H_2O$$

has a high equilibrium constant resulting in a very sharp leading boundary. The tail-end reaction

$$NH_4^+(r) + Na^+(s) + OH^-(s) \rightleftharpoons NH_4OH(s) + Na^+(r)$$

was likewise selected for large equilibrium constant, and a sharp rear boundary is obtained. Thus with carefully packed resin beds the ammonia

moves along the column as a well-defined slug. The reaction at the leading edge generates considerable heat and so imposes a limitation on the concentration of ammonia which can be used. Ten columns in series, each five feet long and four inches in diameter, are employed, and the ammonia zone is cycled around them, the first columns being regenerated before the return of the ammonia. The authors give a complete discussion of all the factors entering into a "laboratory" operation of this kind. Their determination of the equilibrium constant for the isotopic exchange gives

$$N^{14}H_4(r) + N^{15}H_4OH(s) \rightleftharpoons N^{15}H_4(r) + N^{14}H_4OH(s)$$

$$\frac{(N^{15})[N^{14}]}{(N^{14})[N^{15}]} = 1.0257.$$

In the final operation mentioned in the report, 52 moles of ammonia passed through 600 columns; a steady state has been established, and the N^{15}/N^{14} ratio reached unity in the tail of the zone. In this operation fresh ammonia is periodically injected into the slug with the removal of depleted ammonia from the leading edge. It is planned to continue the operation and eventually bleed 99 per cent-plus N^{15} from the tail of the zone.

The work of Spedding's group illustrates well enough the spectacular successes that can be had by the careful application of the principles of chromatography to the simplest possible chemistry. Another extreme, in which a much less sophisticated treatment of a column is needed but in which very much more complex chemistry must be circumvented, is illustrated by the separation of zirconium and hafnium reported by Benedict *et al.* (69). These investigators had much of a preliminary nature to do in studying the stability of their solutions and arranging to care for the niobium daughter of their zirconium tracer before proceeding to the business at hand, namely, a search for a system in which there is an appreciable difference between the selectivity coefficients of zirconium and hafnium. Solutions of HCl, HNO_3, and H_2SO_4 all received attention with the unsatisfying result of producing reasons for previous failures in separation. Recourse was had to complexing agents. Complexes with oxalic acid were found to be too strong to be useful; tartaric acid gave a difference, but at too low a concentration to be easily manageable. It was finally found that a solution 0.091 *M* in citric acid and 0.45 *M* in HNO_3 gave *K* values on Dowex 50 for zirconium and hafnium of 8 and 100, respectively. The column separation turned out almost exactly as expected, and a very clean separation was obtained.

In the separations just described no great concern was required over the characterization of the product. The mass spectrometer served handily for N^{15}. Hafnium gives more trouble but the nuclear chemistry of the hafnium tracers serves well to identify the product. Matters are different when ion exchange methods are applied to the separation of more or less unstable inorganic polymers. Every resource may be needed to prove that material in an elution peak is actually separated from all its congeners. Work of this

nature is well illustrated in the report of Barney & Gryder (70) on the anion exchange purification of sodium tetrametaphosphate. Comment here on the current interest in polyphosphates is superfluous, beyond the remark that the preparation of one such compound in a well-characterized pure state by a carefully prescribed method certainly constitutes an advance. Barney and Gryder prepared more or less impure sodium trimeta- and tetra-

TABLE IV

SEPARATIONS THROUGH ION EXCHANGE

(The numbers refer to the appended bibliography)

CATIONS			
Ag	(71, 72)	K	(87, 88, 89, 90)
Am	(73)	La	(91)
Ba	(75)	Li	(88, 89)
Bi	(72)	Mg	(77, 92, 93)
Ca	(76, 77)	Mn	(82)
Cd	(72, 78)	Na	(87, 88, 89)
Co	(79, 80, 81)	Ni	(79, 81, 82, 83)
Cr	(82)	Pb	(72)
Cu	(71, 72, 81, 83, 84)	Sr	(73, 75, 76)
Fe	(80, 82, 85)	Ti	(94, 96)
Ga	(86)	U	(97, 98, 99, 132)
Ge	(86)	Y	(100)
Hg	(72)	Zn	(78, 80, 101)
In	(86)		

ANIONS			
AsO_4	(102)	ReO_4	(105)
B	(74)	Sb	(95)
BrO_3	(103)	Si	(108)
Cl	(104)	SO_4	(109)
ClO_3	(103)	Sn	(95)
IO_3	(103)	Te	(95)
MoO_4	(94, 105)	Ti	(94, 96)
PO_4	(80, 102, 104, 106, 107)	W	(94)
Rare Earths	(94, 110–116)		
Pt Metals	(117, 118, 119, 120)		

ORGANIC COMPOUNDS			
Acids	(127)	Ketones	(125)
Amino Acids	(121–123)	Peptides	(122)
Galacturonic Acid	(126)	Proteins	(128)
Glutamic Acid	(124)		
Complexing Agents	(129–131)		

metaphosphates and utilized elution from Dowex 1 to bring about the separation. The progress of the experiments was followed by incorporating radiophosphorus in the molecules. It was found that elution with nickel nitrate brought about a separation of the compounds but that the product was certainly impure. A preliminary elution with magnesium nitrate removed the interfering substance (evidently a phosphorus compound) but without separating the tri- and tetrametaphosphates. The nickel elution followed. Recovery of the phosphates from the nickel solution proved somewhat troublesome but was accomplished via the lead salts and a sulfide precipitation. Five entirely independent experiments went into the characterization of the product: overall analysis, electrometric titration, a determination of constancy of solubility, x-ray diffraction, and enzymatic reactions. The results were eminently satisfactory.

Table IV gives a list of elements and compounds for which separations have recently been devised. The utility of the table would certainly be greatly enhanced by the inclusion of statements of conditions, but this has not proved to be feasible.

Nature of Ions from Ion Exchange Properties

The application of ion exchangers to the study of the nature of ions in aqueous solutions has proved itself to be an important extension of the techniques depending on distribution between phases. From a vapor pressure measurement alone a deduction as to ionic nature would certainly be precarious. Distribution of the solute species between two solvents of known dielectric constant produces information which narrows down the possibilities. Distribution into an ion exchanger phase, which contains fixed charges neatly placed to produce large effects, adds significantly to the stock of information. Even though no group, however large, of gross equilibrium measurements can produce a 'final' conclusion, several such taken together give a usefully high probability to an atomistic interpretation. The increment of probability resulting from a consideration of ion exchange equilibria appears to be especially high, both in individual cases and in terms of the number and variety of situations to which it can be applied.

Evidently the study of the distribution of ions between exchanger and solution is also the best technique for establishing the possibility of a separation. All the results considered in this section are basic in planning separations.

The work in this field of Kraus, Nelson, and their colleagues (134 to 141) at the Oak Ridge National Laboratory has reached the stage where it is best described as monumental. The work is so extensive that any account of it without the aid of the periodic table would be confusing. In the table of Figure 1 are summarized the results of Kraus *et al.*, on the distribution of the elements between hydrochloric acid solution and the polystyrene quarternary amine, Dowex 1. The comparative value of these results is enormously enhanced by the simple fact that all the measurements were made

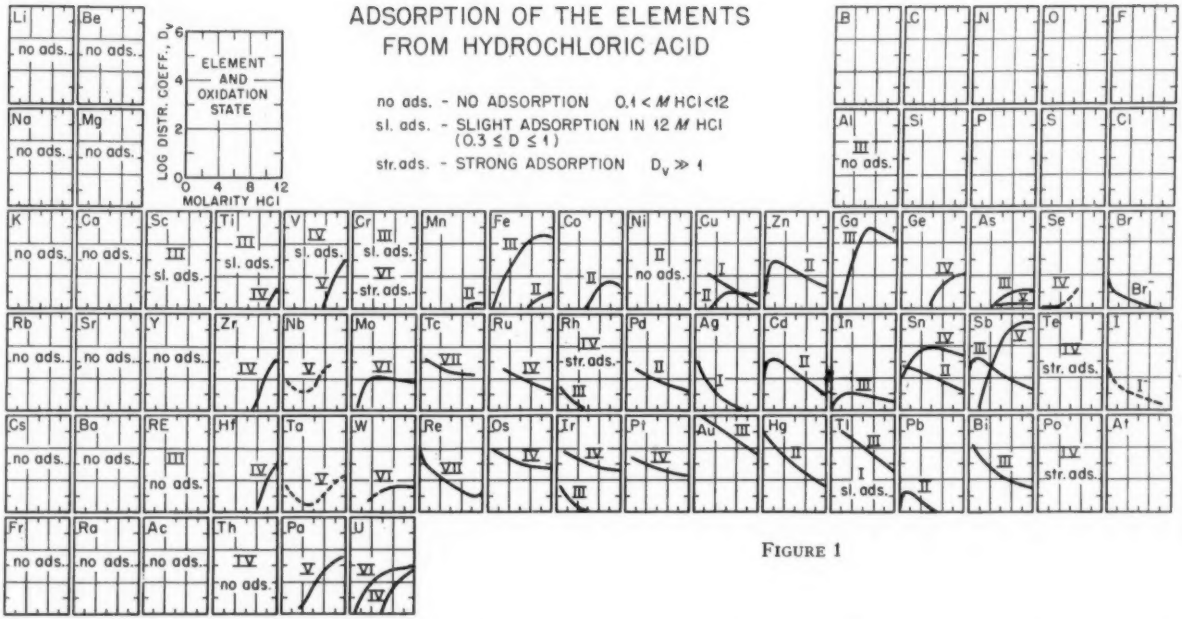

FIGURE 1

* We are much indebted to Dr. Kraus for permission to use this table, P/837 (USA). Some results here indicated are based on unpublished work of Kraus & Nelson, and Kraus & Moore.

† See bibliography (170).

with resin taken from a single large stock. Differences in distribution coefficients certainly occur for different preparations of nominally the same material, as, for example, has recently been shown by Herber *et al.* (133). Effects due to different degrees of cross-linking can be of importance, but these effects are not present in the work of Kraus and Nelson, except in cases where the effects have been the direct object of concern.

The experimental methods used by these workers are well known and need no discussion here.

The character of the arguments by which distribution data are interpreted is well illustrated in the case of chlorauric acid (135). For this substance the nature of the ion in aqueous solutions of hydrochloric acid is considered to be known. Gold chloride is strongly adsorbed by Dowex 1 over a wide range of concentration of hydrochloric acid, from 2 to 16 molal. The distribution coefficient decreases steadily over the entire range, from about 10^6 at 2 molal to 10^4 at 16 molal. The results of the measurements are accurately summarized by the following relation:

$$\log \Gamma_{HAuCl_4} \equiv \log \frac{\gamma'_{\pm HAuCl_4}}{\gamma_{\pm HAuCl_4}} = \frac{1}{2} \log \frac{M_{H^+} M_{AuCl_4^-}}{M_{H^{r+}} M_{AuCl_4^-}} = -\frac{1}{2} \log D \frac{M_{H^{r+}}}{M_{H^+}}$$
$$= -3.24 + 0.75 M_{HCl}$$

Formal molalities are used throughout; no assumptions are introduced. When the equation for Γ_{HAuCl_4} is compared with the similar expression for Γ_{HCl}

$$\log \Gamma_{HCl} = -0.26 + 0.01 M_{HCl}$$

it is apparent that the activity coefficient of the gold species has decreased in the resin nearly a thousand-fold more than the corresponding decrease for HCl, indicating a strong interaction of some sort in the resin phase. At this stage the authors become very careful in their phraseology: "One is tempted to consider this interaction to be primarily between the complex ion $AuCl_4^-$ and the quarternary amine group of the anion exchange resin." The results are consistent with the idea that the species $AuCl_4^-$ exists in solution and in resin over the entire range of concentration and that no other gold species is of importance.

Results as simple as those obtained with gold are rather the exception. Nelson & Kraus (136) have studied the case of lead and bismuth for solutions of hydrochloric acid, nitric acid, and ammonium nitrate. Here matters become very interesting. The distribution coefficient of lead increases sharply with concentration in dilute solutions of hydrochloric acid and passes through a well-defined maximum at approximately 1 molal. In nitric acid solution its behavior is similar. In ammonium nitrate solution the adsorption of lead is small and independent of concentration. Bismuth in hydrochloric acid solution behaves entirely differently. In dilute solutions it is strongly adsorbed and the distribution coefficient decreases steadily with increasing acid concentration but never becomes so low as that of lead.

(Excellent separations of lead and bismuth are easily obtained.) Bismuth in nitrate solutions more nearly resembles lead. A maximum in D is observed in nitric acid, while in ammonium nitrate a steady increase with concentrations is found. The discussion of possible ionic species in this case is necessarily more tentative. Negatively charged chlorocomplexes of lead may be expected to become the dominant species at about 1 molal HCl. Both lead and bismuth appear to form complexes of charge greater than minus one. The sum of evidence at present points to the assignments $BiCl_5^{=}$ and $PbCl_5^{=}$, although especially in the case of lead much uncertainty remains.

Readers interested in details for the application to special problems are referred to the periodic table of Figure 1 and to the original literature.

This account of the work of Kraus *et al.*, on adsorption from hydrochloric acid by no means exhausts the literature on the subject of the contributions of ion exchange to the study of the nature of ions. We may mention a few typical studies. Fronaeus (142) finds evidence for neutral and negative complexes of copper and cadmium. The interesting behavior of the ammonia complexes of copper and silver in their interactions with cation exchangers has received the attention of Stokes & Walton (143). Schufle & Eiland (144) have investigated the halide complexes of indium through a study of equilibria on Amberlite IR-120 and have found evidence for the existence of three different complexes in any one halide system. A system as complex as this certainly needs the attention of different experimental approaches. The hydrolytic behavior of zirconium and hafnium accounts in part for the data of Larsen & Wang (145) in this complex system.

Membranes of Ion Exchangers

Even if it were otherwise desirable, a survey here of the fundamental theory involved in the use, abuse, and behavior of membranes of ion exchangers is rendered quite superfluous by the recent publication of papers presented at the symposium on "Ion Transport across Membranes" (146) held at Columbia University in the Fall of 1953. Discussed at careful length are to be found here the basic theory of the membranes, a model for their action, and a complete survey of experimental and earlier theoretical work in the field.

Kirkwood (146, p. 119) discusses membrane transport phenomena in all generality, for the steady and for an unsteady case, from the point of view of irreversible thermodynamics. A significant result of this approach is a derivation of the equation for the electromotive force, arising from changes in chemical potential across the membrane, in terms of transport numbers defined for the membrane as a whole taken together with the solutions with which it is in surface equilibrium. Thus the theory does not require guesses about transport numbers within the membrane, or a "dissection" of the membrane and a determination of local transport numbers. It is in this sense that the phenomenological character of the approach is most apparent. Implied, however, is the demand for a new experiment for every change in

physical system; the phenomenological approach does not produce calculations of transport numbers. Evidently more detailed theories which give an insight into the fundamental nature of the membranes are still in demand. As always we need useful models.

The transport of ions and of the solvent as registered in the electromotive force are specifically the concern of Scatchard (146, p. 128), who presents the theory of the membrane potential in connection with experiments designed to study the properties of specific membranes. In these experiments a solution whose concentration was varied over a wide range was placed between membranes—on the one side a cation exchanger, on the other an anion exchanger. The "outside" solutions were identical and of fixed concentration. Flowing junctions were employed. The electromotive force of such a combination is given by the sum of the ideal term and those involving transference numbers of the nonexchange ions in the respective membranes and the transference numbers for water. Ideal electromotive forces are found over approximately a thousand-fold change in concentration ratio (for NaCl solutions). The deviations at high concentrations are shown to be largely due to the transfer of water. Deviations at low concentrations remain unaccounted for. As the author points out the study of the properties of the membranes themselves lies in their nonideality. With "good" membranes these deviations are relatively small, and it is difficult to push the experiments to high precision in this regard. The interpretation of the behavior of specific membranes will evidently remain a matter of concern for a long time to come.

Parlin & Eyring (146, p. 103) discuss a model for a membane exhibiting permselectivity and carry out calculations in some detail for fluxes likely to be of significance in a biological membrane. A significant result of their treatment shows, even for the relatively simple model considered, that a constant potential gradient through the membrane does not imply a uniform concentration gradient.

Sollner, Dray, Grim & Neihof (146, p. 144) present a valuable review of the whole field of membrane study with a particularly comprehensive bibliography.

In view of the impossibility of making definitive statements in general terms of the electrochemical properties of specific types of membranes, we shall here merely mention the character of a small part of the work published during the past two years and give an undoubtedly incomplete listing of other work in references (152 to 164).

Wyllie (147) has obtained equations for the multi-ionic potentials of membrane electrodes, and Wyllie & Kanaan (148) have made a comprehensive series of measurements of the bi-ionic potential for a considerable variety of membranes. In this work the results are expressed in terms of intramembrane mobility ratios, which are characteristic of the resin-ion systems considered.

Graydon & Stewart (149) have prepared membranes by the copoly-

merization of propyl *p*-styrenesulfonate with styrene and divinylbenzene and subsequent hydrolysis to the acid. By this means they obtained membranes of different capacities with the sulfonate groups uniformly distributed in the matrix. The electrochemical behavior of these membranes was studied in static experiments with the membranes between solutions of sodium chloride. Membranes showing nearly ideal behavior exhibited steady potentials after two or three changes of solution. The results are discussed in terms of transfer of chloride ion and of water. It was necessary to make some rather drastic assumptions as to ion mobilities in the membranes and activities in the resin phase. The authors point out that the results are best considered as comparisons of their membranes rather than as absolute determinations. Generally water transfer is the more important contributor to nonideality.

The membrane behavior of resins of polyacrylic acid crosslinked with glycol bismethacrylate has recently been studied by Hills *et al.* (150) and by Despić & Hills (151), who have measured potentials and the conductance of the polymers. The conductance determinations were carried out in such a way as to eliminate contact resistances. Potassium ion in these materials may show an equivalent conductance nearly as large as in a water solution of comparable concentration.

Catalysis Produced by Ion Exchangers

The catalysis of chemical reactions by ion exchangers has received relatively little attention during the past two years. Applications in organic chemistry have been cataloged by Helfferich (165), who in a long list summarizes by type reactions which have been studied. Helfferich (166) points out that it may be advantageous in the treatment of results to include explicitly a distribution coefficient for the reacting species.

McAuliffe & Coleman (167) have investigated hydrogen ion catalysis as brought about by acid clays and show that metal ions on the exchange sites of the clays generally are without effect in the reactions. Bernhard *et al.* (168) and Riesz & Hammett (169) have studied this point with a lightly crosslinked polystyrene sulfonate. They find specific effects in ester hydrolysis if quaternary ammonium ions replace hydrogen and summarize the results very simply: "like dissolves like," e.g. a phenyl substituted ion will increase the relative activity of the hydrogen resin for the hydrolysis of a phenyl substituted ester.

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POLYMERS[1]

By Arthur V. Tobolsky

Department of Chemistry, Princeton University, Princeton, New Jersey

In the preceding issue of Annual Reviews of Physical Chemistry (for 1954) under the heading of polymers the general subject of kinetics of polymerization was reviewed. It seems appropriate to discuss for this year's review a specialized topic of this rather broad field. The topic chosen is initiation of polymerization. Two aspects of this subject will be treated under the headings of Part A and Part B. Part A will be a discussion of the rates of initiation in homogeneous vinyl polymerizations for which the initiation and propagation proceed via a free radical mechanism. This subject has been studied quite extensively in my laboratories during the past several years and will be developed below according to the methods I have previously used (1). In Part B a brief discussion will be essayed of some new methods of polymerization which produce stereospecific polymers. These methods of polymerization, associated mainly with the names of Ziegler and Natta, do not proceed via a radical mechanism. Although these new methods of polymerization are just in their infancy, they bid fair to create a major revolution in polymer science and technology.

Part A

The Elementary Steps in Vinyl Polymerization Proceeding via a Radical Mechanism

The simplest kinetic situation for vinyl-type polymerization is obtained when a pure vinyl monomer such as styrene or methyl methacrylate is polymerized under constant temperature conditions through the agency of a radical producing catalyst such as benzoyl peroxide. For a homogeneous reaction the polymer and the catalyst should be soluble in the monomer. Furthermore to avoid complications one should restrict the discussion to the early phases of polymerization (less than 10 per cent of monomer converted to polymer and in some cases even lower conversions). One simplifying feature which makes the study of initial rates very convenient, is that both catalyst and monomer can be assumed to maintain constant concentrations.

The discussion can also be extended to the case where the polymerization is carried out in a solvent which exerts no specific retarding or inhibitory influence on the polymerization except for the fact that it reduces the monomer concentration.

The reaction steps for polymerization under these conditions are:

Decomposition of Catalyst.—

$$\text{Catalyst} \rightarrow 2\mathbf{R}\cdot \qquad 1.$$

The rate of spontaneous homolytic decomposition of catalyst is k_d[Cat].

[1] The literature survey for this review was concluded in February, 1956.

The rate of formation of primary radicals from the catalyst is $2k_d$[Cat].

Initiation of Polymer Chains.—

$$\mathbf{R}\cdot + \mathbf{M} \rightarrow \mathbf{RM}_1\cdot \qquad 2.$$

where **M** refers to monomer.

The rate of initiation will be denoted by R_i. We can also set $R_i = 2fk_d$[Cat] where f is defined as the catalyst efficiency. Obviously f is the fraction of the radicals produced in the primary homolytic cleavage of the catalyst which are effective in initiating polymer chains.

Propagation of Polymer Chains.—

$$\mathbf{RM}_n^{\cdot} + \mathbf{M} \xrightarrow{k_p} \mathbf{RM}_{n+1}^{\cdot}. \qquad 3.$$

It is assumed that k_p is the same for the growth of polymeric species of all kinds. The rate of disappearance of monomer by reaction (3) is $k_p[\mathbf{RM}_n^{\cdot}][\mathbf{M}]$.

Let the total concentration of polymeric radicals of all types be denoted by [**C***].

$$[\mathbf{C}^*] = \sum_{n=1}^{\infty} [\mathbf{RM}_n^{\cdot}]. \qquad 4.$$

Monomer disappears by reactions 2 and 3. The total rate of disappearance of monomer is denoted by R_p (the rate of polymerization) and is given by:

$$R_p = R_i + k_p[\mathbf{C}^*][\mathbf{M}]. \qquad 5.$$

Under almost all circumstances the second term on the right hand side is enormously larger than the first term. The ratio of these two terms is called the kinetic chain length of the chain reaction. The material chain length of the polymer being formed (average degree of polymerization) cannot exceed twice the kinetic chain length. Hence in all cases where high polymers are formed:

$$R_p = k_p[\mathbf{C}^*][\mathbf{M}] \qquad 6.$$

Termination of Growing Polymer Chains.—

$$\mathbf{RM}_n^{\cdot} + \mathbf{RM}_p^{\cdot} \xrightarrow{k_{tc}} \mathbf{RM}_{n+p}\mathbf{R} \qquad 7$$

$$\mathbf{RM}_n^{\cdot} + \mathbf{RM}_p^{\cdot} \xrightarrow{k_{td}} \mathbf{RM}_n + \mathbf{RM}_p. \qquad 8.$$

Two types of termination are possible. The first is combination (eq. 7); the second is disproportionation (eq. 8). The notation $\mathbf{RM}_n$ and $\mathbf{RM}_p$ refers to polymeric chains which no longer have their radical activity.

The rate of disappearance of pairs of radicals by combination and disproportionation respectively is $k_{tc}[\mathbf{C}^*]^2$ and $k_{td}[\mathbf{C}^*]^2$. The rate of disappearance of radicals (Moles per liter per second) by these processes are $2k_{tc}[\mathbf{C}^*]^2$ and $2k_{td}[\mathbf{C}^*]^2$. It is assumed that k_{tc} and k_{td} are independent of the size of the polymeric radicals.

Transfer Reactions.—

The growing polymer radicals can interact with solvent, monomer, initiator or polymer in the following ways:

$$\mathbf{RM}_n^{\cdot} + \mathbf{S} \xrightarrow{k_{tr,S}} \mathbf{RM}_n + \mathbf{S}^{\cdot} \qquad 9.$$

$$\mathbf{RM}_n^{\cdot} + \mathbf{M} \xrightarrow{k_{tr,M}} \mathbf{RM}_n + \mathbf{M}^{\cdot} \qquad 10.$$

$$\mathbf{RM}_n^{\cdot} + \mathbf{Cat} \xrightarrow{k_{tr,Cat}} \mathbf{RM}_n + \mathbf{Cat}^{\cdot} \qquad 11.$$

$$\mathbf{RM}_n^{\cdot} + \mathbf{P} \xrightarrow{k_{tr,P}} \mathbf{RM}_n + \mathbf{P}^{\cdot}. \qquad 12.$$

In the above equations **S, M, Cat** and **P** refer to molecules of solvent, monomer, initiator and polymer respectively. It is assumed that in all cases the radical formed on the right hand side of equations 9 through 12 react rapidly with monomer to start a new polymer chain. In this way the transfer reactions reduce the molecular weight of the polymer but not the rate of polymerization except insofar as the monomer concentration is lowered by the presence of solvent or polymer. If the radicals produced on the right hand side of equations 9 through 12 were slow to react with monomer we would be dealing with a specific inhibitory or retarding effect which we will not consider at this time.

The rates of all the transfer reactions can be summarized by the equation:

$$\textit{Rate of transfer to } \mathbf{X} = k_{tr,x}[\mathbf{C}^*][\mathbf{X}]. \qquad 13.$$

Rates of Initiation: The Fundamental Equations

The two quantities concerning a vinyl polymerization that are directly measurable are the initial rate of polymerization and the number average degree of polymerization. The former can be measured by precipitating polymer and weighing or by following the volume change during the polymerization dilatometrically; the latter can be measured by precipitating the polymer and measuring osmotic pressure of a dilute solution, or more conveniently, by measuring intrinsic viscosity, if the latter has been calibrated with osmotic pressure measurements.

Under the very simplest conditions, if no chain transfer reactions occur and if all termination occurs by disproportionation the following relationship obtains:

$$R_i = \frac{R_p}{\overline{P}_n} \qquad 14.$$

where $\overline{P}_n$ is the number average degree of polymerization. Equation 14 is not generally valid but even in the more general case the rate of initiation R_i under any set of conditions can be determined from measurements of the rate of polymerization and the degree of polymerization.

As in other chain reactions a steady state concentration of active intermediates is rapidly attained. In this case the active intermediates are the growing polymer radicals whose concentration is $[\mathbf{C}^*]$. The steady state

condition is characterized by the fact that the rate of initiative of growing polymer radicals is equal to the rate of disappearance of the growing polymer radicals, i.e.;

$$R_i = (2k_{tc} + 2k_{td})[\mathbf{C}^*]^2. \tag{15.}$$

Eliminating $[\mathbf{C}^*]$ between equation 15 and equation 6 we get the following fundamental relation between the rate of initiation R_i and the rate of polymerization R_p

$$R_i = \frac{2A''}{[\mathbf{M}]^2} R_p^2 \tag{16.}$$

where:

$$A'' = (k_{tc} + k_{td})/k_p^2. \tag{17.}$$

Equation 16 indicates that the rate of initiation can be determined from the rate of polymerization provided that the quantity A'' can be determined. In the next section we will show how a quantity A' closely related to A'' can be determined by measurements of the degree of polymerization as well as the rate. A'' can be calculated from A' provided that the relative rate of combination versus disproportionation can be determined and this subject will also be discussed.

For a catalyzed polymerization the rate of initiation is given by the following formula:

$$R_i = 2fk_d[\mathbf{Cat}] + R_{i,th}. \tag{18.}$$

In the above equation, $k_d[\mathbf{Cat}]$ is the rate of spontaneous first order homolytic cleavage of the catalyst. The factor 2 appears because 2 primary radicals are produced by every spontaneous cleavage (at least for simple catalysts such as benzoyl peroxide). The factor f is the catalyst efficiency, i.e. the fraction of primary radicals which are effective in starting polymer chains. The second term on the right hand side of equation 18, namely $R_{i,th}$ is equal to the rate of purely thermal initiation.

Substituting equation 18 in equation 16 one obtains:

$$R_p^2 = \frac{R_{i,th}}{2A''}[\mathbf{M}]^2 + \frac{f^2d}{A''}[\mathbf{Cat}][\mathbf{M}]^2. \tag{19.}$$

Equation 19 is in good agreement with the empirically observed result for many catalyzed polymerizations which can be expressed as follows:

$$R_p^2 = R_{p,th}^2 + K^2[\mathbf{Cat}][\mathbf{M}]^2 \tag{20.}$$

where $R_{p,th}$ is the purely thermal rate under the given conditions of temperature and monomer concentration and K is an overall rate constant. Equation 20 is usually applied to bulk polymerizations (monomer undiluted by solvents) carried out under varying concentrations of a given catalyst. If the monomer concentration is varied by carrying out the polymerization in a solvent, K may become a function of monomer concentration if the catalyst efficiency f in equation 19 varies with monomer concentration.

If the initiator is effective and is present in appreciable concentration, the contribution of thermal polymerization is negligible and equation 20 becomes:

$$R_p = K[\mathbf{Cat}]^{1/2}[\mathbf{M}]. \qquad 21.$$

Determination of A'

The number average degree of polymerization, $\overline{P}_n$, of the polymer produced at any given moment during homogeneous monoradical catalyzed vinyl polymerization can be calculated from the formula

$$\overline{P}_n = \frac{\textit{Rate of polymerization}}{\frac{1}{2} \times \textit{Rate of formation of chain ends}}. \qquad 22.$$

This gives rise to the following relation for catalyzed bulk polymerizations:

$$\frac{1}{\overline{P}_n} = C_{tr,m} + \frac{A'R_p}{[\mathbf{M}]^2} + \frac{C_{tr,\mathbf{Cat}}R_p^2}{K^2[\mathbf{M}]^2} \qquad 23.$$

where $C_{tr,m}$ is the chain transfer constant to monomer, $C_{tr,\mathbf{Cat}}$ is the chain transfer constant to catalyst, $\overline{P}_n$ is the number average degree of polymerization, and K is the quantity previously discussed. In the absence of chain transfer to catalyst, the quadratic term disappears and A' is evaluated from the slope of a linear plot of $1/\overline{P}_n$ versus R_p. Fortunately catalysts for which chain transfer to catalyst is absent can be found; 2-azobisisobutyronitrile is such a catalyst.

Tobolsky & Offenbach (2) have recently given an accurately determined set of A' values for styrene at temperatures ranging from 0°C., to 90°C. The data fit the following equation:

$$A' \textit{ (Styrene)} = 5.68 \times 10^{-6} \exp (12.46 \text{ kcal}/RT). \qquad 24.$$

Values of A' for methyl methacrylate have been obtained (3) between the temperature of −40°C. and 98°C. The data fit the following equation:

$$A' \textit{ (methyl methacrylate)} = 4.65 \times 10^{-3} \exp (6.93 \text{ kcal}/RT). \qquad 25.$$

The quantity A' is closely related to A'' and is defined in the following way:

$$A' = \frac{2k_{td} + k_{td}}{k_p^2} = A''(1 + x) \qquad 26.$$

$$x = k_{td}/(k_{tc} + k_{td}). \qquad 27.$$

A' obviously lies between A'' and $2A''$ depending upon the relative amount of disproportionation and combination in the termination process. Substituting equation 26 into equation 16 one obtains:

$$R_i = \frac{2A'}{[\mathbf{M}]^2} \frac{R_p^2}{(1 + x)}. \qquad 28.$$

For the initiation produced by the catalyst alone (subtracting the purely thermal initiation) we have from equation 20:

$$R_i = \frac{2A'}{[\mathrm{M}]^2} \frac{R_p^2 - R_{p,0}^2}{(1+x)} = \frac{2A'K^2[\mathbf{Cat}]}{(1+x)}. \qquad 29.$$

Since the quantity x is somewhat difficult to determine as discussed subsequently it is useful to define another quantity $R_i' = R_i(1+x)$. This quantity varies between R_i and $2R_i$ depending on the relative amount of combination and disproportionation (see equation 27). R_i' can be determined directly from A' values (obtained from $\overline{P}_n$ determinations) and K values (obtained from R_p measurements).

$$R_i' = 2A'K^2[\mathbf{Cat}]. \qquad 30.$$

In reference (1) was given equations for R_i' as a function of temperature for the following initiators in styrene and/or methyl methacrylate: benzoyl peroxide, azobisisobutyronitrile, bis 2,4-dichlorbenzoyl peroxide, lauroyl peroxide, bis-p-chlorobenzoyl peroxide, t-butyl hydroperoxide, t-butyl perbenzoate, di-1-naphthoyl peroxide. These results were calculated from polymerization data obtained from literature sources covering twenty years. They should be modified (very slightly) because of the improved A' values given in references (2) and (3). Recently we have obtained data between 60° and 98° for R_i' for di-t-butyl peroxide (DTBP) in both styrene and methyl methacrylate (4). This follows the equation:

$$R_i' = 5.6 \times 10^{14} \exp(-35.0 \text{ kcal}/RT)[\mathrm{DTBP}] \text{moles/liter/sec.} \qquad 31.$$

This result is of particular interest because of the fact that data are available on the gas phase decomposition of DTPB over a temperature range of 350°C. The polymerization data are in general agreement with gas and solution phase decomposition data. Among other simple initiators whose kinetics have been studied by this method during 1955 is hydrogen peroxide (5), reported by Nandi and Palit.

Combination versus Disproportionation

The calculation of rates of initiation from polymerization data through equation 29 to better than a factor of two presumes a knowledge of the relative rates of combination and disproportionation. Although there seems to be a unanimity of opinion that combination is predominant in styrene (6) ($x=0$) there seems to be a wide divergence of opinion in the case of methyl methacrylate as to whether combination of disproportionation is predominant.

There are several ways of measuring the value of x in equation 27. One method is to use a tagged initiator such as 2-azobisisobutyronitrile and to measure the number of end groups in the polymer by sensitive counting methods and also to measure the number average molecular weight of the polymer. The number of radioactive end groups per polymer molecule can thus be determined. If this number is two, then obviously polymer radicals

terminate by combination; if this number is one then the polymer radicals terminate by disproportionation (correction needs be made for a slight amount of chain transfer to monomer).

The molecular weight distribution is different for polymers terminated by combination and disproportionation. If disproportionation and transfer can be neglected then the mole fraction $X(n)$ of n-mers [as shown by Tobolsky & Baysal in reference (7)] is given by the equation:

$$X(n) = np^{n-1}(1-p)^2. \qquad 32.$$

If no combination occurs then the size distribution is given by

$$X(n) = p^{n-1}(1-p). \qquad 33.$$

In the former case (combination important) the ratio of weight average to number average molecular weights is 1·5. In the latter case (disproportionation important) this same ratio is 2·0. This ratio can be determined experimentally to find which termination mechanism obtains (7, 8). Because of this same difference in size distribution the intrinsic viscosity-molecular weight relations for fractionated and unfractionated polymers bear a different relationship for polymers terminated by combination and disproportionation (7).

If termination occurs by disproportionation only and transfer is small, half the polymer molecules will have an unsaturated end group. These molecules may possibly depolymerize more rapidly than the others; the unsaturated end group serving as a point of initiation (9), as was pointed out by Grassie and Vance. In such a case we might expect half of the polymer to depolymerize more rapidly than the other half, as was in fact claimed by these authors.

It has been claimed that the number average molecular weight versus intrinsic viscosity relation for unfractionated polymers prepared in the presence of chain transfer agents and in the absence of chain transfer agent is the same (10). This would tend to favor disproportionation as the termination step since both transfer and disproportionation produce the same molecular weight distribution.

If the literature of the past few years concerning disproportionation versus combination in methyl methacryalte is reviewed, it appears that papers are evenly divided between these two mechansims. As an example one might quote the disparate results obtained using radioactive initiators by Arnett & Peterson (11) on the one hand and Melville, Bevington & Taylor (12) on the other hand. Some of the most recent literature favors disproportionation as the preponderant reaction. I myself have strong reservations about this even in the face of the most recent evidence. The value of R_i' that I obtain for various initiators such as benzoyl peroxide, di-t-butyl peroxide and 2-azobisisobutyronitrile are nearly the same in the two monomers, styrene and methyl methacrylate. It is to be presumed that the rates of spontaneous cleavage of these initiators is nearly the same in both mono-

mers. If $R_i' = R_i(1+x) = 2f(1+x)k_d[\mathbf{Cat}]$ is the same in both monomers, and if x is zero in styrene and $x=1$ in methyl methacrylate, then the catalyst efficiency must be half as large for benzoyl peroxide, di-t-butyl peroxide and 2-azobisisobutyronitrile in methyl methacrylate as in styrene. This seems to me to be too surprising a coincidence to let the matter rest in favor of disproportionation.

Catalyst Efficiencies

Inasmuch as the methods just described permit one to calculate the rate of initiation of polymer chains (to at worst with an uncertainty factor of two if the relative rates of combination and disproportionation are unknown), it is clearly of interest to compare this quantity with the rate of production of primary radicals from the primary homolytic cleavage of the catalyst (initiator) molecules. In many cases the total rate of disappearance of catalyst molecules (which is an experimentally measurable quantity), arises from two sources: the primary cleavage into radicals plus a radical induced chain decomposition of the catalyst. In certain cases, such as that of benzoyl peroxide, kinetic methods have been successfully used in analyzing the total rate of decomposition into its two component parts [method of Nozaki & Bartlett (13)]. There are however some simpler cases where the total rate of decomposition of catalyst is exactly equal to its rate of spontaneous homolytic fission. One notable case is 2-azobisisobutyronitrile, whose decomposition has been studied extensively by many workers. This substance decomposes by a first order rate law at very nearly the same rate in all solvents, and is unaffected by the presence of radical inhibitors. The rate of decomposition has been studied by measuring the rate of nitrogen evolution (14, 15, 16) and by following the disappearance of the compound spectrophotometrically (17).

Because the rate of primary radical production is unequivocally equal to twice the measured rate of catalyst disappearance, this initiator provides an excellent case study for determination of catalyst efficiency. The catalyst efficiency f is defined as follows:

$$f = \frac{\textit{Rate of primary radical production}}{\textit{Rate of initiation of polymer chains}} = \frac{2k_d[\mathbf{Cat}]}{R_i} \qquad 34.$$

where k_d is the first order rate constant of the primary cleavage and the factor two appears because 2 radicals are formed upon cleavage.

The efficiencies of several widely used catalysts are fairly high (between 0.50 and 1.0) according to some of the latest estimates (1). This is perhaps not surprising since these catalysts (such as benzoyl peroxide and 2-azobisisobutyronitrile) have passed the tests of practical utility. However the deviation of catalyst efficiency from a figure of exactly unity has some very interesting theoretical implications. If very inactive radicals are produced we may expect to find initiators with very low values of catalyst efficiency, and possibly we may find initiators that are efficient in resonance stabilized

monomers such as styrene but inefficient in non-resonance stabilized monomers such as vinyl acetate.

According to Walling and others one reason for the deviation of catalyst efficiency from unity even in efficient catalysts may arise from recombination of the two radicals produced from the same initiator molecule before they have time to diffuse sufficiently far apart from one another (18). This is known as the so-called "cage effect" and an attempt has been made by Noyes to calculate the magnitude of this primary recombination from basic principles (19). Furthermore, if the radicals are inactive toward addition to monomer, secondary recombination may occur between radicals arising from different catalyst molecules. This may give rise to very low efficiencies.

Our latest figures for the efficiency of initiation by 2-azobisisobutyronitrile in styrene and methyl methacrylate using the method for measuring R_i described in the above sections is 60 per cent between 30° and 80° (1, 20). This figure is in good agreement with that obtained by Bevington (21) by using radioactive 2-azobisisobutyronitrile as the initiator and measuring the rate of appearance of radioactivity in the polymer. The efficiency of this catalyst has also been studied by Bevington as a function of monomer concentration in benzene-styrene mixtures and found to be independent of monomer concentration down to very low values (21), at which point the efficiency drops rapidly. If we assume combination in methyl methacrylate, we get the same value of 2-azobisisobutryonitrile efficiency as in styrene (20).

The stable free radical 2,2 diphenylpicrylhydrazyl has been used to measure the rate of radical production for such catalysts as benzoyl peroxide and 2-azobisisobutyronitrile. The technique involves measuring the rate of decolorization of the characteristically colored solutions obtained with this stable free radical. It has been questioned whether this technique truly measures the rate of primary production of radicals; the proposition has been put forward by Walling (18) and by Hammond *et al.* (22) that the hydrazyl cannot react sufficiently rapidly with the primary radicals to prevent primary recombination. Recent work by Lyons & Watson (23) however indicates that some of the results obtained with diphenylpicrylhydrazyl may be somewhat in error because of formation of complexes of this material with solvents used in recrystallizations.

The most convincing experimental results proving the existence of a "cage effect" in reducing the efficiency of polymerization below unity are the studies of Szwarc on the decomposition of acetoyl peroxide (25). For this peroxide it was shown that decomposition in solution always gives rise to ethane even in the presence of the most powerful radical inhibitors. On the other hand the formation of ethane in the gas phase can be completely suppressed by iodine. Formation of ethane in solution is believed to be due to the primary recombination of two acetate radicals from the same peroxide molecule before they have a chance to escape the "cage" or lose their identity.

In the gas phase there obviously is no cage effect. Szwarc also gives a theoretical discussion of initiator efficiency (25).

Chain Transfer to Initiator

Equation 23 when cast in the following form enables one to determine chain transfer to initiator (26, 26a):

$$\frac{1}{\overline{P}_n} - C_{tr,m} - \frac{A'R_p}{[\mathbf{M}]^2} = C_{tr,cat}\frac{[\mathbf{Cat}]}{[\mathbf{M}]}. \qquad 35.$$

The chain transfer constant of styrene with benzoyl peroxide was determined by Mayo, Gregg & Matheson (24) and shown by these authors to correlate with the rate of induced decomposition of benzoylperoxide in this solvent. Transfer constants of benzoyl peroxide, t-butyl hydroperoxide and cumene hydroperoxide in styrene and methyl methacrylate were obtained by Johnson, Baysal & Tobolsky (26, 26a) and also by Chang & Walling (27). Inasmuch as chain transfer to initiator produces polymers of lower molecular weights, this process must be taken into account in the practical production of polymers.

Diradical Initiation

For many years the thermal and photo polymerization of monomers such as styrene were believed to proceed via a diradical initiation. In 1945 I became interested in this problem and pointed out that a true diradical initiator could be obtained by utilizing a ring peroxide or a ring azo compound as the initiator (28). I felt that it would be of great interest to compare the R_p vs $\overline{P}_n$ relations for polymerizations initiated by monoradical producing catalysts such as benzoyl peroxide, for diradical producing catalysts such as monomeric (ring form) phthaloyl peroxide, and for thermal and photo-initiations. The relation between $1/\overline{P}_n$ and R_p for monoradical initiated polymerization has already been given; in the absence of chain transfer to the initiator (as with 2-azobisisobutyronitrile) the relation is:

$$\frac{1}{\overline{P}_n} = C_{tr,m} + \frac{A'R_p}{[\mathbf{M}]^2} \text{ monoradical line.} \qquad 36.$$

A plot of $1/\overline{P}_n$ versus R_p gives a straight line in these cases which we have called the monoradical line. If by means of a diradical initiator we were able to produce a growing diradical polymer chain, and if the possibilities of ring formation and transfer to the catalyst are specifically neglected, we pointed out that the corresponding relationship between $1/\overline{P}_n$ and R_p is (26):

$$\frac{1}{\overline{P}_n} = C_{tr,m} + \frac{x}{1+x}\frac{A'R_p}{[\mathbf{M}]^2} \text{ diradical growth} \qquad 37.$$

(x varies between zero and one, depending on the relative importance of combination and disproportionation).

Much to our surprise the point for thermal and photo-polymerization in styrene and methyl methacrylate fell on the monoradical line (25, 26),

i.e., the same line as is obtained by using 2-azobisisobutyronitrile as the initiator. We concluded therefore that both thermal and photo-initiation probably proceeded via a monoradical initiation (26, 26a, 29).

In the case of photo-initiation it was not hard to believe that ultraviolet light might fragment the monomer rather than excite the double bond to a diradical state. It was hard however to understand how monoradicals could be formed in thermal polymerization until this was elucidated by later kinetic work described below.

If thermal polymerization proceeded via diradical initiation, it was clear that at least some rings would be formed by recombination of radicals at the ends of the same polymer chain. Johnson & Tobolsky indicated that the formation of rings in such a situation would very measurably affect the molecular weight distribution and the viscosity molecular weight relationships (26). Howard discussed the kinetics of ring formation during thermal polymerization, assuming diradical initiation, from a theoretical point of view (30). He showed that ring formation is favored if the diradical concentration is low and that the rings that are formed would tend to be among the low molecular weight species of the molecular weight distribution. Zimm & Bragg, also assuming that thermal polymerization proceeded via a diradical initiation emphasized that most of the diradicals formed would tend to go to rings of small size because of the rapidity of combination compared to propagation (31). This viewpoint is undoubtedly correct. However Zimm & Bragg also contended (31) that a few of these diradicals were converted to monoradicals by chain transfer with the monomer, and that these monoradicals grew to chains of high molecular weight. This mechanism for explaining the appearance of high polymer in thermal polymerization can not be correct. In the first place one should expect that, if it were true, the addition of small quantities of compounds very active in chain transfer would lead to enhanced production of high molecular weight polymer during thermal polymerization. That this is not so is attested by the experiments of Mayo, Gregg & Matheson (24) and of Russell & Tobolsky (32). Secondly, if the mechanism of thermal high polymer formation proposed by Zimm & Bragg were correct, the relative weight of small rings compared to total polymer formed would be well over twenty per cent. Again this is not found to be the case experimentally.

Some other papers in this field have further clarified the situation. Russell & Tobolsky found that the inhibitor 2,2-diphenylpicrylhydrazyl reacted with styrene at 60° at about sixty times the rate at which long chain polymer was initiated (33). This same result was independently obtained by Chapiro *et al.* (34). It was tempting to assume that the high rate of disappearance of DPPH was due to reaction with diradicals which otherwise would form rings; the high polymer being formed in an independent monoradical initiated reaction (33).

At just the same time Mayo found that during the thermal polymerization of styrene a few per cent of ring compounds were formed which he

deemed to be a reaction proceeding independently of the formation of high polymer; he presumed that the rings were probably formed from diradicals (35). The rates and the activation energy of the reaction forming rings appeared to agree quite well with the rate of DPPH disappearance found by Russell & Tobolsky (33). Mayo also found that the kinetics of thermal initiation of styrene (in brombenzene solution) was termolecular, which would explain the formation of monoradicals (35).

I am at present not fully convinced that the formation of rings found during the thermal polymerization of styrene arises from diradicals or that the rapid disappearance of DPPH found under these conditions is due to a reaction with diradicals. I remember well a conversation with the late Prof. E. H. Farmer in 1947 in which I asked him whether the ring compounds formed from dienes and olefins at high temperatures arose from diradicals; his answer was that the structures of these rings where known was such as to suggest a polar mechanism. Also it is perhaps questionable whether if a diradical were formed in styrene it would have time to react very appreciably with DPPH before recombination of the radical ends occurred.

Considering that the high polymer formed during thermal polymerization does not arise from diradicals, it becomes all the more interesting to find a true diradical source for initiation. My first attempts to produce an unequivocal diradical initiator date back to 1945–1946, when with Shah & Leonard I attempted to prepare the monomeric ring form of phthaloyl peroxide (36). Using the method that Baeyer & Villiger (37) had described for preparing this compound we found that we obtained a polymeric chain peroxide instead. This compound does not give a simple diradical when heated but breaks into two fragments each of which can initiate a polymer chain: the polymeric peroxide attached to the end of the chain can however dismute again and start a new polymer chain growing in the other direction, etc. Using polymeric phthaloyl peroxide as an initiator of styrene polymerization we found that we obtained a product whose molecular weight increased with increasing conversion (36).

Polymeric phthaloyl peroxide has recently been used by Woodward & Smets to obtain block copolymers (38). Polystyrene polymer prepared with this initiator has been dissolved in methyl methacrylate. The active polymeric peroxide fragments at the end of the polystyrene chain have thereupon initiated the addition of polymethyl methacrylate "blocks" to the original polymer.

The first undoubted simple diradical initiator employed in polymerization was the cyclic ethyl ether disulfide ($S{-}CH_2{-}CH_2OCH_2CH_2S$) used in conjunction with light in the wave length region 3000–4000 A° by Russell & Tobolsky (32). Under the same conditions dibutyl disulfide was shown to initiate monoradical polymerization of styrene and methyl methacrylate. The cyclic disulfide however produced no high polymer at all even though it was shown that the disulfide linkage was being destroyed. It was inferred

that any diradicals formed were producing small rings rather than polymer.

Recently Overberger *et al.* have produced a simple cyclic azo compound and have used it under conditions where its thermal decomposition rate was measurable, but found it produced no polymerization in styrene (39). Straight chain azo compounds decomposing at similar rates will produce polymer and again it is inferred that the diradicals produced from the cyclic azo compound either recombine immediately or add one or two monomer units and then recombine to form small rings. Monomeric phthaloyl peroxide has also been prepared recently, and it too produces no high polymer (40).

An interesting sidelight on the work with cyclic peroxides is that Russell & Tobolsky found that the transannular terpinoid peroxide ascaridole must decompose to monoradicals in the presence of light, because under these conditions polymerization is produced in methyl methacrylate (32). Furthermore under varying light intensities and/or peroxide concentrations the variation of $\overline{P}_n$ and R_p obeyed the monoradical line. Similar results were later found by Zand & Mesrobian using ascaridole and dihydroascaridole as thermal initiators of polymerization at higher temperatures (41).

Free Radical Initiation by Some Special Initiating Systems

During 1955 the use of disulfides as initiators of polymerization was reported by Kern (42) and by Ferington & Tobolsky (43). It was found that many well known rubber accelerators of disulfide structure will also initiate polymerization, the initiation being surprisingly rapid even at temperatures as low as 60° and 80°. However a careful study of the kinetics of polymerization induced by tetramethylthiuram disulfide showed that this substance acted as both an initiator and a retarder, the retarding effect being marked at high concentrations (43). In as yet unpublished results the rate of initiation produced by tetramethylthiuram disulfide at various temperatures was found to be given by the equation

$$R_i' = 4{\cdot}8 \times 10^{14} \exp(-31{\cdot}6 \text{ kcal}/RT)[\text{TMTD}].$$

The substance tetramethylthiuram monosulfide was also found to be an initiator of polymerization, both thermally and photochemically, but its rate of thermal initiation was slower than that obtained with the disulfide.

As an interesting sidelight, one might expect a fair amount of chain transfer to initiator when using disulfides as initiators. The transfer reaction cleaves the disulfide at the S—S bond as shown by Tobolsky & Baysal (44) and also by Stockmayer, Howard & Clarke (45). These authors proved that ring disulfides actually copolymerize with vinyl monomers such as styrene and vinyl acetate via a chain transfer reaction. Extensive studies on disulfides as chain transfer agents have recently been published by Pierson, Marvel & Costanza (46, 47).

Although many studies have been made on polymerization induced by high energy radiation, few complete kinetic studies in homogeneous organic media have been published.

Seitzer *et al.* (48) have shown that the initiation of polymerization by

β-rays proceeds by a radical mechanism. A polymerization was carried out by exposing an equimolar mixture of styrene and methyl methacrylate to a β-ray source. Analysis of the copolymer showed it to be 51 per cent styrene and 49 per cent methyl methacrylate, which is diagnostic of a radical mechanism. The polymerizations were also inhibited by oxygen and free radical inhibitors. Finally, the relation between R_p and $\overline{P}_n$ fits the radical mechanism.

By polymerizing styrene and methyl methacrylate in the presence of numerous solvents, Seitzer & Tobolsky were able to use the rate of polymerization as a kind of chemical clock and thus determine the G-values produced by β-rays in these solvents (49). (G-values are here defined as the number of initiating radicals produced per 100 C.V. of radiation absorbed.) G-values were obtained for twelve solvents, ranging from 10.2 for carbon tetrachloride to 0.220 for styrene. The relative order of G-values for these solvents correlated very well with those previously obtained by Magat *et al.* (50) using gamma rays. However our values were in all cases roughly 1/9 of those obtained by Magat *et al.* I recently have received a preprint of a publication from the Brookhaven laboratories by Ballantine & Mesrobian (51), in which the work on polymerization of monomers in solvents via gamma rays was repeated. The G-values that these workers obtain for gamma rays agree very well in absolute magnitude with the values we obtained with β-rays and disagree numerically with the Magat *et al.* values.

Since the pioneering studies of Horner (52), and Horner & Schwenk (53) showing that very fast initiation could be produced with the system benzoyl peroxidedimethyl aniline in vinyl monomers, a number of studies have been made on this sytem. Meltzer & Tobolsky (54) found that for this catalyst activator system in styrene, the rate of initiation at 0°C. was proportional to the product of the concentration of dimethyl aniline and the concentration of benzoyl peroxide. O'Driscoll & Tobolsky (3) have found that the rates of initiation produced by this sytem in methyl methacrylate between 0°C. and $-40°$ is given by the equation

$$R_i' = 5.4 \times 10^{11} \exp(-12.8 \text{ kcal}/RT)[\text{DMA}][\text{Bz}_2\text{O}_2].$$

At these low temperatures the contribution to the initiation produced by the unactivated primary cleavage of the benzoyl peroxide is negligible. At 30° Imoto *et al.* (55) have proposed that the observed rate of polymerization of methyl methacrylate induced by dimethyl aniline-benzoyl peroxide is given by:

$$R_p = C_1[\text{Bz}_2\text{O}_2]^{0.5} + C_2\{[\text{Bz}_2\text{O}_2][\text{DMA}]\}^{0.5}.$$

Actually, since it is the rates of initiation which are additive the correct expression is:

$$R_p^2 = C_1^2[\text{Bz}_2\text{O}_2] + C_2^2[\text{Bz}_2\text{O}_2][\text{DMA}].$$

Imoto and co-workers also studied the rates produced by this system in styrene (56). They find that at 50° the production of radicals initiating polymerization accounts for only 25 per cent of the decomposition rate of the

peroxide. The fact that other (probably polar) reactions between amine and peroxide are occurring which do not produce initiating radicals and that the efficiency of the initiation is low has also been confirmed by Walling (57). The low efficiency is in accord with the fact that polymerizations of styrene induced by the DMA—Bz_2O_2 system reach about 20 per cent conversion and then stop because of depletion of the peroxide.

Imoto and co-workers have also studied the polymerization of vinyl chloride (58) and acrylonitrile (59) by the system DMA—Bz_2O_2. The polymerizations are more complex because the polymer precipitates in monomer.

The rates of decomposition of substituted benzoyl peroxides with dimethyl aniline have been studied (60) and interpreted in terms of the Hammett equation. The rates of decomposition of benzoyl peroxide by variously substituted tertiary aromatic amines have been studied by Lal & Green (61).

Part B

New Catalyst Systems Producing Stereospecific Polymers

The discovery of new catalyst systems which produce stereospecific vinyl and diene polymers has opened up new vistas in polymer chemistry; the scientific and industrial consequences of these new methods are of the greatest importance. During the last few months of 1955 some of these developments, which hitherto were enshrouded in industrial secrecy, were published in the scientific journals. I shall attempt only a brief account of these developments inasmuch as a true scientific perspective will be achieved only after the passage of more time. By the time this section is in print many major developments will probably have occurred which will definitely "date" this section.

Ziegler *et al.* (62) discovered that ethylene could be polymerized at low pressures (1 atm. or less) and low temperatures (room temperature and higher) to obtain polymers in the molecular weight range 20,000–3,000,000. These polymers differ from the polyethylene prepared by the conventional high pressure radical initiated process in that they are essentially linear polymethylenes with no long chain or short chain branching. Because of this the new polyethylenes are more crystalline, and have a higher density and greater rigidity than the "old" polyethylenes.

The Ziegler catalyst is a combination of aluminum triethyl and a cocatalyst such as titanium tetrachloride which are mixed together in an inert solvent (63). A precipitate forms and the ethylene is bubbled through the slurry. Ziegler *et al.* believe that the polymerization proceeds by an anionic mechanism (62).

A similar type of polyethylene was produced independently by the Phillips Petroleum Company using an entirely different type of catalyst, namely a mixture of chromium oxide and aluminum oxide.

Meanwhile Ziegler continued his work on other olefins, and research work was carried out by various companies who licensed the Ziegler patents. Goodrich-Gulf announced the synthesis of an essentially all cis-1,4-poly-

isoprene made by polymerizing isoprene with a Ziegler type catalyst (64). This rubber was essentially identical to natural rubber. Here then was a synthesis of a stereospecific polymer, duplicating a natural product, which was accomplished by these new catalysts! Goodyear also announced the synthesis of all cis-1,4-polyisoprene by means of Ziegler type catalysts (65). To make the situation even more dramatic, Firestone announced the synthesis of all cis-1,4-polyisoprene by means of an entirely different catalyst, finely dispersed metallic lithium (64).

Natta, using a Ziegler type catalyst, announced the synthesis of a crystalline polystyrene (66). X-ray studies of this material indicated that the optically active carbon atoms along the chain (those to which the phenyl rings are attached) are probably arranged in patterns in which long sequences of successive *d*-configurations are followed by long sequences of successive *l*-configurations (67, 68). Perhaps these sequences may run the length of an entire molecule. These polymers were called isotactic polymers by Natta and are to be contrasted with the usual vinyl type polymer prepared by radical initiation in which *d* and *l* configurations are randomly arranged. The existence of isotactic polymers was foreshadowed by Schildknecht, who showed that two very different types of vinyl ether polymers could be obtained by different types of initiators, and attributed the difference in the properties of these polymers to specific arrangements of the *d*, *l* sequences along the chain (69). Huggins had suggested this possibility on purely theoretical grounds even earlier (69a).

Natta and co-workers have also used other types of heterogeneous catalysts such as the Cr_2O_3—Al_2O_3 types to obtain stereospecific or "isotactic" polymers. In addition to polycrystalline polystyrene they have also obtained polycrystalline polypropylene and polybutylene. Also all trans polybutadiene and all cis polybutadiene were obtained (70, 71), and also all 1,2 polybutadiene.

Natta proposes a mechanism (70, 71) for the production of stereospecific polymers in which the monomer is attached to the solid catalyst surface. A new monomer unit then breaks the previous monomer-surface bond, forms a new bond with the surface and also attaches to the previous monomer unit. During this process the entering monomer unit can be oriented by the surface in such a way as to produce stereospecific or isotactic polymers.

It is my belief that the production of stereospecific polymers need not necessarily be confined to heterogeneous catalysts and therefore depend on surface reactions. During homogeneous ionic polymerizations (both cationic and anionic) the growing polymer ions are always closely accompanied by the counter ions (gegen ions) from the catalyst. These gegen ions may very well influence the addition of monomer units and thus produce stereospecific polymers.

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KINETICS OF REACTIONS IN SOLUTION[1]

By Richard M. Noyes

Department of Chemistry, Columbia University, New York, N. Y.; Department of Physical Chemistry, The University, Leeds, England

This review is concerned with kinetics of homogeneous reactions in liquid phase, including photochemistry, but excluding heterogeneous catalysis, reactions at electrodes, nucleation processes, and effects of ion-exchange resins and of ionizing radiations. Even with these restrictions, an incomplete perusal of the literature produced over 700 references or more than enough to fill the allowed space with a mere bibliographical listing. Each paper deals with improving a technique of kinetics, with the development of a satisfactory theory of chemical reactivity, or with the use of kinetics to aid in elucidating the detailed mechanism of a specific reaction; although these different objectives are not mutually exclusive. This review attempts to cover contributions to the first two of these objectives and to mention some mechanistic conclusions (whether or not based on kinetic data) that seem of more than routine interest to students of chemical reactivity. The reviewer has chosen his mechanistic examples strictly on the basis of personal prejudice but has tried to cover a wide range of types. Enzymatic reactions have been omitted because of a feeling of incompetence to judge the significance of contributions.

Experimental Techniques

Although the year saw no compendium comparable to the recent Faraday Society publication (1), interest has continued in very fast ionic reactions. Eigen & Schoen (2) have calculated rates of ionization and recombination from the effects of brief, intense electrical fields on conductivities of aqueous solutions. Wiesner (3) has discussed the use of polarographic techniques to follow the rates of very rapid homogeneous reactions, and Rüetschi (4) has shown how the method can be extended to measure the rates of ionization of acids that are not themselves reducible. Delahay *et al.* (5) have also discussed polarographic techniques and have concluded that voltammetry at constant current is still more promising; the apparatus is described by Reilley *et al.* (6).

Since ionic equilibria are also sensitive to pressure effects, Bies (7) has used ultrasonic absorption and relaxation frequency to measure the rate of dissociation and recombination of $MgSO_4$ as a function of dielectric constant of water-dioxane mixtures.

The ionized and unionized forms of electronically excited naphthols have different fluorescent spectra, and the ionization constants differ from those of the ground states. Weller (8) cleverly uses the pH dependence of the

[1] The survey of literature pertaining to this review was completed in December, 1955.

fluorescent spectra to calculate the rates of ionization of the excited forms.

For reactions with half-lives of the order of a few seconds, Bell *et al.* (9, 10) have continued to apply the thermal maximum method involving the temperature change during reaction under non-adiabatic conditions, and Elving & Lakritz (11) have used their rapid conductometric method. Fierens *et al.* (12) have discussed a more conventional conductometric procedure for measuring second order rate constants to 3 per cent.

The detection of free radical intermediates continues to be of interest. Several techniques have been reviewed by Abrahamson (13). Norman & Porter (14) have trapped radicals at low temperatures in rigid solvents and have measured their absorption spectra. Ingram *et al.* (15) have used paramagnetic resonance absorption to detect radicals in the same rigid solvents. This technique (16) and chemical scavengers (17) have measured trapped radicals in linear polymer. Bengough & Melville (18) have continued to use their thermocouple method to follow the nonstationary state in radical polymerization reactions.

Pitts *et al.* (19) have shown how the accuracy of the conventional uranyl oxalate actinometer can be improved by oxidizing blank and irradiated solutions with ceric ion and using differential spectrophotometry to determine the extent of reaction. Copestake & Uri (20) have proposed the trioxalato complex of cobalt (III) as an alternate actinometric material, and Baxendale & Bridge (21) have investigated several complexes of iron (III) for extension of actinometric procedures to the visible spectrum.

A symposium has been published on the application of kinetic methods to analytical problems (22). Other techniques for kinetic measurements have included continuous absorption of evolved gas by Barret (23), application of ice calorimetry by Smith (24), and use of infrared absorption by Slowinski & Claver (25) to follow polymerization.

Mathematical Techniques

There are so many possible combinations of consecutive and competitive reactions that no completely general integration procedure has ever been developed, but Tobin (26) has discussed the integration of various combinations of reversible and irreversible first and second order reactions. DeTar (27) has treated parallel half and first order reactions. Talât-Erben (28) discusses the maximum amount of intermediate in consecutive first order reactions.

Many publications treat the special case of two consecutive second order reactions with one reagent common to both. Yvernault (29) discusses the difficult problem of evaluating both rate constants from measurements in the early stages of reaction, and Bak (30) discusses the general case. The classic method of Frost & Schwemer (31) for stoichiometric ratio of reactants has been simplified by Cooke & Gerrard (32) when the rate constants are considerably different. It has been extended by Widequist (33) to any ratio of reactants by changing the time variable, and Morrow (34) discusses a series approximation.

Noyes (35) has treated the situation in which reactive fragments are produced in pairs and may either recombine with each other by diffusion or may react with a scavenger molecule in the solution. To a first approximation, the probability of reaction with scavenger varies as the square root of its concentration. Roy, Hamill & Williams (36) have independently reached the same conclusion and have shown that I^- ions can scavenge I atoms that would otherwise react with the specific I_2^- ions from which they were separated by photochemical dissociation of I_3^-.

Kinetics of free radical polymerizations continue to attract interest. Howe (37) has avoided the usual steady state approximation in developing a general mathematical treatment, but the equations have not been applied to experimental data. Magat (38) has treated the case in which some radicals are removed by burial in polymer instead of by reaction with each other, but Breitenbach & Schindler (39) have objected to the treatment. Burnett & Loan (40) have treated solvent participation in a polymerization, and Palit *et al.* (41) have shown how to modify treatments if chain transfer reagents react with initiator radicals. Palit (42) has also derived general equations for copolymerization kinetics with application to the special case in which the values of different termination constants cause the rate to go through a minimum as composition is changed. The copolymerization problem has been treated in other ways (43, 44) and has been extended to three-component systems by Blackely, Melville & Valentine (45).

Unfortunately, a whole new language is developing with the quantitative attack on enzyme reactions, even though the kinetic problems appear to be identical with those of complex-forming ions in inorganic chemistry. Somewhat different steady state treatments of inhibited systems have been developed by Beers (46), Bernhard (47), and Christiansen (48). Problems connected with the validity of the steady state approximation have been considered by Beers (49), Laidler (50), and Morales (51). Laidler (52) has attempted to generalize the effect of pH on enzyme reactions, and Cavanaugh *et al.* (53) have treated a system in which an inhibitor complexes with the substrate instead of with the enzyme. Niemann and co-workers (54) have attempted to apply more quantitative methods to recalculate a mass of kinetic data taken from the literature on enzyme reactions.

Seitzer & Tobolsky (55) have developed the theory of polymerization induced by β-particles from a point source if they are absorbed exponentially and if radicals do not diffuse far from their point of genesis. Bunton *et al.* (56) have examined the kinetics of exchange reactions in systems exhibiting significant isotope effects and have shown that first-order approach to equilibrium will always be observed except perhaps for some hypothetical cases involving large concentrations of stable isotopes of light elements. Huyberechts *et al.* (57) have developed conventional statistical expressions for the reliability of Arrhenius parameters calculated from kinetic data of known accuracy.

Nonstructual Factors Influencing Reactivity

Rates of reaction depend upon several factors in addition to the purely chemical nature of the reactive species. Any satisfactory theory of chemical reactivity must account for the various effects.

Effect of pressure.—The partial molar volume of the transition state is calculable from rates at different pressures. Burris & Laidler (58) have discussed this little explored field and shown the positive correlation of $\Delta V^{\neq}$ and $\Delta S^{\neq}$ in ionic reactions. David, Hamann, & Lake (59) have studied the methanolysis of ethyl chloride up to 30,000 atmospheres.

Effect of temperature.—Hyne & Robertson (60) have treated deviations from the Arrhenius equation as measures of $\Delta C_p^{\neq}$ but find that experimental precision is not sufficient to select the best empirical expression. It is not clear to the reviewer how an apparent positive $\Delta C_p^{\neq}$ can be distinguished from two parallel paths with different activation energies.

Effect of isotopic mass.—Theory and examples of effects involving hydrogen isotopes have been reviewed by Gold & Satchell (61) and by Wiberg (62). Deuterium substitution in the solvent often has little effect (63), but Swain & Ketley (64) use such an effect in chlorination by HOCl to claim that the rate-determining step is $H_2OCl^+ \rightarrow H_2O + Cl^+$. Adamson & Basolo (65) studied aquation of $Co(NH_3)_5Cl^{++}$ and $Co(ND_3)_5Cl^{++}$ in both H_2O and D_2O and found the change of solvent affected rates in opposite directions for the two ions. Additional examples are included below of mechanistic interpretations of isotope effects.

Effect of magnetic fields.—Gelles & Pitzer (66) find that the paramagnetic Dy^{+3} ion has a slightly abnormal catalytic effect on decarboxylation reactions, and Gelles & Reed (67) find that the effect is greater for a $^{12}C—^{12}C$ than for a $^{12}C—^{13}C$ bond. These results suggest that magnetic moments as well as masses may contribute to isotope effects.

Effects of solvent and neutral salt.—Kinetic theory is still a very long way from understanding effects of changing medium on polar and ionic reactions, but several experimental and theoretical studies have appeared. Tommila and others in Helsinki have conducted extensive studies of medium effects on solvolyses of esters (68), alkyl halides (69), and sulfonic esters (70), and on the decarboxylation of acids (71). Koivisto (72) has shown the marked similarity of solvent effects on the heat of ionization of an acid and on the energy of activation for the process $E + H_2O \rightarrow EOH^{-\neq} + H^+$ where $EOH^{-\neq}$ is the transition state for alkaline hydrolysis of an ester.

Amis (73) has discussed his purely electrostatic theories of solvent effects and applied them (74) to ester hydrolyses, and Bell & Lindars (10) have found electrostatic considerations sufficient for a semi-quantitative treatment of acidic and basic hydrolyses of a positively-charged ester. Wiberg & Shryne (75) have emphasized the large entropy effects of polar reactions in nonpolar solvents.

However, Smith & Leffler (76) have demonstrated that electrostatic explanations are not sufficient and that specific effects are involved during a

solvolysis when the acetone in an aqueous mixture is partly replaced by another organic reagent. Caldin & Peacock (77) from studies of the reaction $B+HN{=}NOOH \rightarrow BH^+ + N_2O + OH^-$ have classified solvents as aromatic, aliphatic, and hydroxylic, and have proposed certain generalities applicable to each class.

Swain *et al.* (78) have made a monumental attempt to correlate a mass of solvolytic reactions in terms of one parameter dependent only on the compound and another dependent only on the solvent. Only slightly better results are obtained (79) with four parameters instead of two. Objective criteria are developed (78) for the general problem of "goodness of fit" of empirical relations of this sort. Wilputte-Steinert & Fierens (80) maintain that the treatment with only one solvent parameter is unsatisfactory unless only bond-breaking is important in the transition state.

Spieth & Olson (81) studied salt effects on solvolyses in various concentrations of aqueous acetone and developed empirical correlations. Nash & Monk (82) separated common ion and ionic strength effects for the reaction of *t*-butyl bromide in the same solvent, and calculate a charge separation of 2.6 Å in the transition state. Grunwald & Cristol (83) show that at different neutral salt concentrations the rate of a reaction may actually be affected in opposite directions by adding ethanol to water.

Rates of radical reactions are less affected by solvent changes. Das *et al.* (84) found little influence of solvent on rate constants for propagation of polymerization, although constants for chain transfer to solvent naturally varied considerably. Boozer *et al.* (85) found little evidence for solvent effects on the reactivities of RO_2 radicals during air oxidation.

Effect of acidity.—The correlation of rate with the Hammett H_0 function continues to be important for mechanistic diagnosis of the involvement of water molecules. Taft *et al.* (86) have used this argument to show that no water molecule is bound to the transition state for hydration of ordinary olefins but that the rate-determining step is probably the rearrangement of a proton complex to a carbonium ion. However, transfer of a proton to α,β-unsaturated aldehydes is rate-determining. Gold & Satchell (87) have shown that rearrangement of a positive complex is also rate-determining in exchange of deuterium ion with aromatic molecules, and Gold & Hilton (88) have shown that acetic anhydride hydrolyzes by dissociation of the conjugate acid. Bell *et al.* (89) determine that a water molecule is present in the transition state for acid-catalyzed ester hydrolysis, but Bunton *et al.* (90) show that it is not involved in breaking the R^+—OH_2 bond in *sec*-butyl alcohol, even though a molecule of solvent water reacts from the rear of the carbon atom before the leaving water molecule can be displaced.

The H_0 scale has been extended to mixtures of acetic and sulfuric acids by Noyce & Pryor (91). Kuivila (92) finds that the reaction of hydrogen peroxide with benzeneboronic acid does not exhibit any of the conventional correlations with acidity in either perchloric or sulfuric acids.

Attempts have been made to develop an acidity function for reactions of

the type $ROH+H^+ \rightarrow R^+ + H_2O$. Gold (93) and Deno *et al.* (94) are not in complete agreement on the best form to use.

Mechanisms of Inorganic Reactions

The Chemical Society has produced an excellent little volume (95) discussing several inorganic reaction types.

Very rapid ionic reactions.—Eigen *et al.* (96) have used their electrical impulse method (2) for several rapid proton transfers. The rate constant (97) of 1.3×10^{11} liter/mole sec. for the reaction $H_3O^+ + OH^- \rightarrow 2H_2O$ is presumably close to the maximum that will ever be discovered in solution. The formula $H_9O_4^+$ is interpreted (98) as the best description of a hydrated proton. Weller (99) uses his fluorescent method (8) to demonstrate general basic catalysis for the alkaline ionization of excited naphthol.

Gerischer (100) and Flengas (101) obtain very different rates for the dissociation of $Cd(CN)_4^{=}$.

Nonoxidative reactions of complex ions.—It has not always been clear whether substitution reactions of complex ions involve a prior dissociation or participation by the substituting group. Studies by Grantham *et al.* (102) of the exchange of chloride with $PtCl_4^{=}$, by Hamm & Perkins (103) on the malonate complexes of Cr(III), and by Pearson, Basolo *et al.* (104) on hydolysis of Co(III) complexes are all interpreted in terms of prior dissociation (*SN*1). Ingold (105) discusses evidence for duality of mechanism.

Stranks (106) and Holden & Harris (107) have studied exchange reactions and isotope effects of carbonate ion with Co(III) complexes having either one or two available sites for complexing, but Saito & Lazard (108) have questioned the validity of some of the isotope effects.

From comparative rates of racemization and exchange, Brintzinger *et al.* (109) conclude that the dipyridyl complex of iron(II) racemizes intramolecularly. Davies & Dwyer (110) support this interpretation but claim racemization of the nickel complex involves dissociation. Postmus & King (111) discuss rates and mechanisms involving the Cr(III) thiocyanate complex. Goodenow & Garner (112) show that the tungsten cyanide complexes do not exchange with radiocyanide.

"Electron transfer" reactions.—Many exchange and redox reactions of metal ions involve net electron transfer, although detailed mechanisms are not always clear. The literature has been reviewed by Dainton (113) and by Zwolinski, Marcus & Eyring (114). Reynolds & Lumry (115) make proposals about the special role of water molecules.

Garner and co-workers have observed homogeneous or induced exchange in the anion systems $IrCl_6^{-2}$—$IrCl_6^{-3}$ (116) and $W(CN)_8^{-3}$—$W(CN)_8^{-4}$ (117) where electron transfer seems plausible. Cohen, Sullivan & Hindman (118) find the slower exchange in the cation system NpO_2^{++}—NpO_2^+ is accelerated by Cl^-, which can act as a bridging ligand and perhaps undergo transfer as an atom in the process. Two-electron transfer in the system Tl^{+3}—Tl^+ is apparently accelerated by OH^- (119), but Penna-Franca & Dodson (120)

find a complex effect of CN^-. Betts (121) concludes the net reaction $2Fe(III) + U(IV) \rightarrow 2Fe(II) + U(VI)$ is initiated by a one-electron transfer forming an intermediate U(V).

Taube (122) has examined various anions as bridging and nonbridging ligands for electron transfer between Cr(II) and Co(III) and has concluded that transfer may also be facilitated by anions that do not serve as bridges in the transition state.

Oxidations involving metal ions.—Medalia (123) has reviewed the principles of induced reactions as applied to analytical chemistry. Baxendale (124) has proposed oxidation products of hydrazine as a test of how many electrons are transferred to the reagent in a single step.

The mechanisms of acid permanganate oxidations are becoming clearer. If manganous ion is present, it reduces permanganate to Mn(III), and this is the active species in subsequent reactions. Adler & Noyes (125) propose that this reduction to Mn(III) can induce oxidation of oxalate in two-electron transfers. Waters *et al.* have used polymerizable monomer to follow radicals produced by one-electron transfer to Mn(III). α-Keto (126) and α-hydroxy (127) carboxylic acids [and presumably oxalate (125)] form radicals that react with another Mn(III), but ketones (126, 128) react only in the enolic form producing radicals that are then destroyed by reaction with each other. Cullis & Ladbury (129) find the rate of oxidation of toluene is accelerated by electron donating groups. Wiberg & Stewart (130) find that benzaldehydes are oxidized by at least two very different mechanisms depending on pH.

From a study of the apparent exchange between permanganate and manganous ions, Happe & Martin (131) report that at least 40 per cent of the MnO_4^- may disappear before any solid MnO_2 is formed. The nature of the intermediate is not clear.

Higginson & Wright (132) note that hydrazine is oxidized by ferric ion to form the products predicted (124) for one-electron transfers, but Speakman & Waters (133) find rather surprisingly that alkaline ferricyanide oxidizes the enolic forms of aldehydes and ketones without forming radical intermediates capable of initiating polymerization. Studies by Baxendale & Magee (134), by Saldick & Allen (135), and by Santappa (136) support the proposal that free OH radicals are formed in the photodissociation of $FeOH^{++}$. Good & Purdon (137) even find some evidence for thermal oxidation of water in ferric chloride solutions.

Kwart & Francis (138) have pointed out the analogies between elimination reactions and oxidation of secondary alcohols by chromic acid. The effect of sustituents on oxidation of $C_6H_5CH(CH_3)OH$ is opposite to that predicted by the simple picture but supports the pre-equilibrium formation of a chromate ester. Kaplan (139) has used isotope effects to indicate that C—H bond rupture is involved in the rate-determining steps for oxidation by Cr(IV) and Cr(V) intermediates, although these species show less isotopic discrimination than Cr(VI).

Nord (140) has measured the rapid air oxidation of cuprous chloride and shown that Cu^{++} is the only active species needed to explain the oxidation of ascorbic acid catalyzed by copper salts. Hargreaves & Sutcliffe (141) propose identical one-electron transfer mechanisms for the oxidation of formaldehyde by cobaltic and ceric ions.

Reactions of oxygen and inorganic peroxy compounds.—Controversy has raged concerning the reactions of hydrogen peroxide and iron salts. Abel (142) has reviewed the literature. George (143), Koefoed (144), and Christiansen (145) have interpreted the data as requiring an electron transfer between two iron ions, one of which is a peroxy complex like $FeOOH^{+}$. Cher & Davidson (146) find somewhat different kinetics for the oxidation of ferrous ion in phosphoric acid and observe copper salt catalysis similar to that treated by Nord (140). Barb *et al.* (147) find that hydrogen peroxide reacts with the ferric complex of $\alpha:\alpha'$-dipyridyl (dipy) and with the ferrous complexes containing one and two (but not three) dipy.

Hughes & Martin (148) find that oxidation of selenious acid by hydrogen peroxide induces decomposition of the peroxide, but there is no accompanying exchange between selenite and selenate.

Persulfate apparently can decompose by the radical ($S_2O_8^{=}\rightarrow 2SO_4^{-}$) and nonradical ($HS_2O_8^{-}\rightarrow HSO_4^{-}+SO_4$) processes. Bawn & Margerison (149) find that diphenylpicrylhydrazyl will trap the radical species SO_4^{-} and OH (derived from it) but will not react with SO_4. They also find that silver ion reacts by $Ag^{+}+S_2O_8^{=}\rightarrow Ag^{++}+SO_4^{-}+SO_4^{=}$ and that cupric ion catalyzes decomposition less efficiently and with complex kinetics. Levitt & Malinowski (150) find that SO_4 is the species oxidizing isopropyl alcohol and point out that alcohols and many other organic species are oxidized preferentially by neutral or positive reagents capable of a two-electron transfer. The picture is somewhat complicated by the observation of Fronaeus & Östman (151) that no more than one cerous ion is oxidized by each persulfate that decomposes; either this reagent reacts only with neutral SO_4, or SO_4^{-} and OH are formed simultaneously in the primary radical process.

Activation of molecular hydrogen.—Halpern & Peters (152) have found that cupric acetate or perchlorate can homogeneously catalyze reduction of several oxidizing agents by hydrogen. The reactions are zero order in oxidizing agent and proceed at the same rate per oxidizing equivalent as Cu_2O would otherwise be formed. Mercuric ion is the only other species showing similar catalytic ability. Wright *et al.* (153) claim that Cu^{+} rather than Cu^{++} is the active species in organic bases as solvents.

Displacement reactions on sulfur.—Exchange and other studies of the polythionates by Fava *et al.* (154) are consistent with the equilibrium process $^{-}O_3SS_nSO_3^{-}+S^{*}O_3^{=}\rightleftarrows {}^{-}O_3SS_{n-1}S^{*}O_3^{-}+SSO_3^{=}$ where n is 2 or more. The individual rate constants increase with increasing n. Cecil & McPhee (155) suggest a similar mechanism for the process $RSSR+SO_3^{=}\rightarrow RS^{-}+RSSO_3^{-}$, although the kinetics are complex for pH below 9.

Masters & Norris (156) propose a simultaneous transfer of $O^{=}$ and Cl^{-} to

explain the exchange of $SOCl_2$ with liquid SO_2.

Miscellaneous inorganic reactions.—Bunton *et al.* (157) claim N_2O_3 is the intermediate involved in the exchange of nitrous acid with water. Downs & Johnson (158) find that three of the chlorine atoms in PCl_5 exchange with the element more rapidly than the other two. Fialkov & Kagan (159) present kinetic evidence that H_3PO_2 can exist in two tautomeric forms. Clusius & Effenberger (160) use isotopic nitrogen to demonstrate the following reactions: $NH_2^- + ON'N'' \rightarrow H_2O + NN''N'^-$ (80 per cent) $+ NN'N''^-$ (20 per cent) $NH_2SO_3H + HN'O_3 \rightarrow H_2SO_4 + H_2O + NN'O$. $NN'N^- + N''O_2^- + 2H^+ \rightarrow H_2O + NN''O + NN'$.

Effects of Structure on Organic Reactions

General considerations.—Hammond (161) has proposed that when reactants and products differ considerably in energy, the one of higher energy will more closely resemble the transition state for reaction. Therefore, when alternative reactions are possible, endothermic processes will always favor thermodynamically stabler products, but reactions of unstable intermediates need not show any correlation with thermodynamic stability of products. Russell & Brown (162) find this principle applicable to the rationalization of relative reactivities in several radical abstraction reactions. van Helden & Kooyman (163) apply different considerations to abstractions by atomic chlorine.

Reactions in conjugated systems.—Only in aromatic systems do people dare to test quantum mechanical calculations by experiment. Fierens *et al.* have measured rates of nucleophilic substitution (164) and of ester hydrolysis (165) for several derivatives of polycyclic compounds. The rates show reasonable correlations with calculated localization energies and indices of free valence and autopolarizability, but failures of complete agreement between experiment and theory suggest that steric and other effects are also involved. Sixma (166) has compared localization energies with reactivities of several aromatic amines and has concluded that inductive effects on reactivity are more important than resonance. Melander (167) has calculated reactivities in the thiophene system.

Radical reactions are less influenced by structural effects. Greenwood (168) points out the good correlation of molecular orbital calculations with relative reactivities of 9-substituted anthracenes and at *ortho* and *para* positions of benzene derivatives. Experiment and theory differ on the direction of the small effect at *meta* positions. Kooyman (169) has made experimental and theoretical tests of the effect of the conjugated groups —N=N— and $>C=N-N=C<$ on reactivities of aromatic systems with radicals. Radical substitutions have been reviewed by Nelson (170).

The Hammett equation is used as a more empirical correlation of aromatic reactivities. Leffler (171) notes that validity independent of temperature requires $\Delta S^{\neq}$ to be a linear function of $\Delta H^{\neq}$, and Fierens and co-workers (172) claim that such an equation will hold only for reactions in which either

bond making or breaking predominates almost to the exclusion of the other. Brown (173), Kuivila (174), and co-workers discuss the Hammett equation as an over-simplification, and Brown & Horowitz (175) propose to extend it to ortho substituents by a suitable choice of reference reaction. Brown & McGary (176) point out that the selectivity of a reagent between *meta* and *para* positions in toluene is related to its selectivity between toluene and benzene, more reactive reagents being generally less selective. Wilmarth & Schwartz (177) apply the Hammett equation to the dissociation of substituted tetrazanes into hydrazyl radicals.

Nucleophilic aromatic substitutions have been studied by workers with Bunnett (178), Hammond (179), Miller (180), and others. Fierens & Halleux (181) have attempted to generalize apparent discrepancies depending on whether or not bond breaking contributes much to the transition state. They also quote an example in which steric hindrance is more important in the ground than in the transition state.

There have been many attempts to separate nonsteric influences. Rooda *et al.* (182) note the $(CH_3)_2NO$ group can only influence reactions by induction without resonance. Roberts and co-workers (183) find that only inductive and field effects are important in the attack of NH_2^- on aromatic hydrogen, and de la Mare (184) also regards induction most important. Rates of reaction of acid derivatives are influenced in peculiar ways by α, β double and triple bonds. These effects have been studied in three countries (185, 186, 187) and interpreted in terms of resonance, inductive, and field effects.

Reactions in saturated systems.—Ingold and co-workers at University College have carried out the most extensive experimental (188) and theoretical (189) study yet attempted on substitution at a saturated carbon atom. They have considered almost all possible combinations for the reaction $Y^- + RX \rightarrow YR + X^-$ where X and Y may each be Cl, Br, or I and where R may correspond to any possibility from $n=0$ to 3 in the systems $(CH_3)_nH_{3-n}CCH_2$— and $(CH_3)_nH_{3-n}C$—. Relative energies and entropies of activation were calculated and compared with measurements in dry acetone. The correlation is sufficient to indicate a considerable understanding of the factors influencing rates of reactions of this type.

Nucleophilic substitutions have long been separated into the *SN*1 and *SN*2 categories, although Swain has maintained a unitarian attitude. Wilputte-Steinert, Fierens & Hannaert (172) now propose a trinity of idealized reaction types designated as *SN*1 (like solvolysis of $(C_6H_5)_3CBr$) where the rate is determined entirely by bond breaking, *SN*2 (like isotopic exchange of an alkyl bromide with bromide ion) where bond making and breaking are equally important in the transition state, and *SN*2 (limiting) (like alkaline hydrolysis of an ester), where the rate is determined entirely by bond making. The classifications are not rigid, and intermediate situations are permissible.

Rates of substitution reactions are influenced by the nature and solvation of the entering and leaving groups. Swain & Dittmer (190) show that several

amines do not show the same relative behavior in substitution that they do in reacting as bases, and Hawthorne, Hammond & Graybill (191) show that cyanide is less effective in substitution reactions than would be expected from its oxidation potential; they ascribe the discrepancy to resonance stabilization of cyanogen. Wiberg (192) finds that the difference in reactivity of OH^- and OOH^- is almost entirely an entropy effect; the peculiar nature of aqueous hydroxide ion may be involved. Swain & Kreevoy (193) discuss solvent effects involved in ionic substitution reactions, and Anantaraman (194) shows that electrophilic reagents help different reactions to different extents.

Kornblum *et al.* (195) discuss substitution reactions by "ambident" species like nitrite and enolate ions having alternative sites for potential reaction. A carbonium ion will tend to react with the position of greater electron density, while *SN*2 reaction will involve the site of lower electronegativity and will produce the thermodynamically more stable product.

It has been difficult to separate steric and other effects in compounds undergoing reaction. Kreevoy & Taft (196) have confirmed that hydrolysis of compounds like $R_1R_2C(OC_2H_5)_2$ involves a rate-determining bond fission in the conjugate acid. They reason that steric requirements in the ground and transition states will be nearly identical, so changes in R_1 and R_2 will affect the rate only through changes in polar and hyperconjugative effects. It has not previously been possible to assign numerical values to these influences. Brown & Cahn (197) have tried to relate steric strains in transition states to those in molecular addition compounds of similar dimensions and have concluded that the effects of increasing methyl substitution in alkyl groups can be explained on steric grounds without requiring invocation of induction. Brown & Moritani (198) discuss direction of elimination in branched systems as determined by electromeric and steric effects. Space prohibits reference to several other studies of effects of structure on reactivity to substitution.

Winstein & Holness (199) have proposed a kinetic procedure for determining the relative amounts of different conformations of cyclohexane derivatives. The procedure suggests valuable applications, although this reviewer is not yet convinced of its validity.

Effects of neighboring orbitals.—Doering & Hoffmann (200) used deuterium to follow the attack of alkali on ions of the type $M(CH_3)_4^+$ where M is N, P, As, or Sb. The rate increases on going up the periodic table from Sb to P, but the nitrogen compound is very much less reactive than any of the others. The results are interpreted as indicating that removal of a proton is facilitated by the availability of vacant d-orbitals on the central atom.

Eaborn & Jeffrey (201) propose that the ease of substitution of I^- for Cl^- in compounds of the type R_3SiCH_2Cl is attributable to participation of vacant orbitals from silicon in the transition state.

Studies with norbornenyl (202) and cholesteryl (203) systems show that the π-orbitals of neighboring double bonds may have considerable influence in speeding the departure of a negative group.

Other Studies of Organic Reactions

Substitution reactions.—Burwell (204) has reviewed the cleavage of ethers. Coleman & Fuoss (205) discuss the kinetics of quaternization of a polyvinyl pyridine where the rate is slowed by the electrostatic effects of reaction at neighboring positions. Nitrate esters may solvolyze to alcohols, olefins, or ketones. Cristol *et al.* (206) and Baker *et al.* (207) rationalize the possible reactions.

The *SN2'* process $Y^- + CH_3CH{=}CHCH_2X \rightarrow CH_3CHYCH{=}CH_2 + X^-$ is not common, but England (208) has been able to compare it with direct substitution by using isotopic bromines for *X* and *Y*. Gazith & Noyes (209) cite evidence supporting their previous contention that radical reagents like iodine atoms can bring about this sort of rearrangement easily. They also propose that the allylperoxy radical, CH_2CHCH_2OO, can react easily with other radicals with loss of molecular oxygen.

Carbonium ions and ion pairs.—Dostrovsky & Klein (210) show that a $(CH_3)_3C^+$ ion is 20 to 30 times more apt to react with water to form alcohol than to form olefin. Roberts & Yancey (211) use carbon-14 to show that the classical structure $(CH_3)_3CC^+(CH_3)_2$ is stable with respect to a proposed methyl bridge between the two carbons, but Bonner & Collins (212) find rapid rearrangement of phenyl groups in a similar ion, and Collins (213) reports the amount of free carbonium ion character determines relative migration tendencies of phenyl and hydrogen. Brown & Jungk (214) discuss methyl migrations in the isomerization of xylenes.

Beringer & Schultz (215) and Russell & Brown (216) both propose that in the dark $RBr + Br_2 \rightarrow R^+Br_3^-$ and that this ion pair may react with more bromine either by substitution with inversion or to form dibromide. Beringer & Gindler (217) discuss the kinetics of ion pair reactions, and Swain *et al.* (218) furnish spectral evidence of an ion pair.

Goering & Silversmith (219) have made several studies of the system

Racemization by interchange of the double bond with X can take place in the ion pair R^+X^- without separation sufficient for X to become attached to the other side of the ring, much less to escape completely. If X is *p*-$O_2NC_6H_4COO$, they find the acid-catalyzed reaction involves no racemization except by complete dissociation (220); incipient dissociation here does not involve fragments of opposite electrical charge.

Addition and elimination reactions.—The reaction $RCHXCHXR + 3I^- \rightarrow RCH{=}CHR + 2X^- + I_3^-$ is of importance when X is a halide. Different workers (221, 222, 223) have obtained evidence that the first and rate-determining step is often but not always *SN2* displacement by iodide ion.

Miller & Shkapenko (224) propose that base-catalyzed addition to mul-

tiple bonds involves preliminary addition of an ion like RO^-. Lynch & Pausacker (225) propose an interesting mechanism for the addition of oxygen to an olefin by perbenzoic acid.

Formation and hydrolysis of esters.—Esters may be hydrolyzed by several mechanisms, depending among other things on whether bonds to alkyl or acyl groups are broken. Alkyl-oxygen fission has been reviewed by Davies & Kenyon (226), and several examples have been studied by Stimson (227). Bunton *et al.* (228) have used oxygen-18 as an aid in identification and have found that the methyl and tertiary butyl esters of 2,4,6-triphenylbenzoic acid can be made to illustrate all known types of carboxyl esterification and hydrolysis.

Alkaline hydrolysis often involves preliminary addition of OH^- to the carbonyl carbon, and this step may be reversible or rate-determining. Bender & Ginger (229) discuss factors influencing the fate of the intermediate formed by such an addition, and Pearson *et al.* (230) consider the related basic cleavage of activated ketones where an additional acid-base reaction of the intermediate is involved.

Bunton *et al.* (231) have shown that both C—O and P—O bond fission may occur in the hydrolysis of organic phosphates, and Kumamoto & Westheimer (232) and Cooke & Gerrard (32) consider the kinetic effects in these reactions.

Other organic reactions involving acids and bases.—Caldin & Long (233) have measured rate constants down to −78.5°C. for the rapid reactions of nitro aromatic compounds with ethoxide ion. Apparently, both additions and proton transfers can occur.

A symposium on the hydroxycarbonylation reaction (234) includes a discussion by Bell & Rand (9) of the mechanism of hydration of acetaldehyde. Noyce *et al.* (91, 235) studied the similar condensation of benzaldehyde and acetophenone.

Zollinger (236) has shown that the azo coupling reaction $ArN_2^+ + RH + B \rightarrow ArN{=}NR + BH^+$ involves reversible addition of ArN_2^+ and rate-determining removal of the proton. Ballester (237) has reviewed the mechanism of the Darzens condensation. Wiberg (238) concludes that the mechanism previously proposed for the benzoin condensation is not consistent with the isotope effects he observes.

Reactions of organometallic compounds.—The cleavage of diphenyl mercury with acid (239), the abstraction of a proton by phenyl lithium (240), and the reduction of a ketone by $NaBH_4$ (241) all show kinetics that are first order in each of the reacting species. Baddeley (242) has reviewed aspects of the Friedel-Crafts reaction.

Lithium compounds and Grignard reagents abstract hydrogen by reactions like $RLi + HS \rightarrow RH + LiS$. Isotope effects depend considerably on the S—H bond. Thus Gronowitz & Halvarson (243) find $k_H/k_T = 6$ for removal from the 2 position in thiophene, but Assarsson (244) finds only 1.7 for removal from water. Wiberg (238) finds CH_3OD may actually react faster than

CH_3OH indicating that hydrogen is bound more strongly in the transition state than in the ground state.

Jenny & Roberts (245) quote interesting evidence for

as intermediate in the reaction of C_6H_5F and C_6H_5Li.

Isomerization reactions.—The benzidine rearrangement, $C_6H_5NHNHC_6H_5 \rightarrow NH_2C_6H_4—C_6H_4NH_2$, exhibits general acid catalysis with two protons in the transition state. Hammond & Grundemeier (246) show from absence of an isotope effect with *para*-substituted deuterium that the rate-determining step involves addition of the second proton to the molecule rather than the subsequent rearrangement.

Davies & Evans (247) have studied several *cis-trans* isomerization reactions in solution. Just as for gas phase reactions, they find the rates fall into two groups characterized by high and low values of the Arrhenius parameters A and E.

Non-polymeric radical reactions.—Free radicals are often produced by dissociation of compounds like RN=NR. Cohen & Wang (248) have generalized the kinetic effects of successive addition of phenyl groups to the carbon attached to nitrogen. For reasons discussed by Noyes (35), Bevington (249) finds that not all dissociations produce radicals capable of reacting with chemical scavengers. However, Talât-Erben & Bywater (250) find no discrepancy between the two methods of measurement. Ferrington & Tobolsky (251) form radicals by thermal dissociation of an activated S—S bond.

The quantitative detection of radicals is difficult. Hammond, Boozer *et al.* (252) show that several scavengers give concordant results but that diphenylpicrylhydrazyl is sometimes unsatisfactory, and Bengough (253) points out the danger of using a polymerization induction period. Franzen (254) proposes N,N,N′,N′,-tetraethyl-*p*-phenylenediamine as a stable detector of radicals.

Szwarc (255) and co-workers appear to have developed an interesting technique for studying the reactivities of methyl radicals. Acetyl peroxide decomposes $CH_3CO_2—O_2CCH_3 \rightarrow 2CH_3 + 2CO_2$. Sometimes both methyls from the same molecule react with each other, but those that escape this fate can be followed by competitive reactions. Studies include reactions with aromatic hydrocarbons (256), quinones (257), and ethylenes (258). The initial decomposition can be photosensitized with anthracene (259). Hey (260), Simamura (261), and co-workers have measured relative reactivities of phenyl radicals and compared them (262) with methyl reactivities. Radical additions to anthracenes are discussed by Farenhorst & Kooijman (263).

Skell & Woodworth (264) find that the radicals formed by addition of CCl_3 to *cis* or *trans* butene-2 undergo isomeric equilibration before reacting with $BrCCl_3$, but Bristow & Dainton (265) find that polymeric radicals formed from the same olefins can add SO_2 before the end group loses its isomeric identity.

Gazith & Noyes (209) have studied the exchange of benzyl iodide and iodine over a range of 10^6 in relative concentrations and find benzyl radicals and iodine atoms show about equal reactivity toward each other. Russell (266) finds big differences in reactivity of peroxy radicals from cumene and tetralin.

Onyszchuk & Sivertz (267) present an unusually detailed kinetic treatment of the photochemical addition of mercaptans to olefins. Pieck & Steacie (268) have studied the liquid phase photolysis of acetone and compared with gas phase. Overberger & Lapkin (269) find even large diradicals cyclize so easily that they doubt there can be significant diradical initiation of polymerization.

Polymerization reactions.—During the past year, there have been a number of publications on polymerization kinetics, including synthesis of block copolymers, detection of trapped radicals, and establishment of mechanisms of termination in several cases. Valentine (270) has prepared a much more thorough review than is possible here.

Miscellaneous organic reactions.—Anbar & Ginsburg (271) have reviewed the mechanisms of reactions of organic hypohalites. Brand (272) has proposed NO_3 as the active species in the oxidation of cyclohexane by N_2O_5. Bowen & Tanner (273) discuss reactions of electronically excited anthracene and propose that oxygen can catalyze the singlet-triplet transition.

Calvin and co-workers have examined the photolysis of cyclic disulfides (274) and have considered the whole photosynthetic cycle (275) as illustrating the negative feedback principle involved in the kinetics of living processes.

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KINETICS OF REACTIONS IN GASES[1,2]

By George Porter

Department of Chemistry, University of Sheffield, England

General Overview

The particular interest which attaches to investigations of reactions in the homogeneous gas phase is attributable to the fact that one is able to study chemical reactivity in its simplest form. The more detailed our investigations the more it becomes evident that, even in their simplest form, chemical reactions are remarkably complex. The experimental work reported in the year under review provides numerous examples of complications in reaction mechanisms which have been previously accepted as illustrating some particular elementary mechanism.

In unimolecular decomposition the complexities caused by concurrent radical and molecular mechanisms and the transition to second order kinetics at low pressures had long been known and understood in principle. In addition, however, it now seems probable that the details of the collisional activation processes may have to be considered more specifically for each inert gas which is used to effect the energy transfer. Hinshelwood and his colleagues (1 to 4) have shown, both for the thermal decomposition of hydrocarbons and of nitrous oxide, not only that there are very specific effects of various inert gases on the rate of decomposition but that their influence cannot be explained purely on the grounds of maintenance of a stationary equilibrium of a single activated state. It seems that at least two types of activated state play a part in each case. In the nitrous oxide decomposition the second activated state may be the triplet state—and indeed this is to be expected on the grounds of spin conservation as was pointed out many years ago by Herzberg (5). Whether the triplet state is responsible in hydrocarbon decomposition also and whether the same complexities will be found in other unimolecular decompositions remains to be seen, but it is clear that a much closer enquiry into the structures of the excited states of molecules and the transfer of energy between them will be essential to a complete understanding of activation processes.

In the theory of bimolecular reactions Bodenstein's reaction between hydrogen and iodine has played a conspicuous role as a straightforward four-centre second order process. However the data of Bodenstein himself show that such a description is not complete; in particular, there is an abnormally high temperature coefficient of the activation energy of the reaction (21

[1] The survey of literature pertaining to this review was completed in December, 1955.

[2] The following abbreviations have been used in this chapter: P.E. (potential energy); M.O. (molecular orbital).

cal./mole/degree). Benson & Srinivasan (6) have reconsidered the data in terms of the possibility of a concurrent chain process

$$I_2 + M \underset{k_3}{\overset{k_2}{\rightleftharpoons}} 2I + M - 35.6 \text{ kcal.}$$

$$I + H_2 \underset{k_5}{\overset{k_4}{\rightleftharpoons}} HI + H - 32.8 \text{ kcal.}$$

$$H + I_2 \underset{k_7}{\overset{k_6}{\rightleftharpoons}} HI + I + 35.5 \text{ kcal.}$$

If $k_5 \ll k_6$ this gives for the first stages of the reaction

$$\frac{d[HI]}{dt} \approx 2k_4[H_2][I_2]^{1/2}K_{23}^{1/2}.$$

If we now include the true bimolecular process

$$\frac{d[HI]}{dt} = k_6[H_2][I_2](I + R)$$

where

$$R = \frac{2k_4K_{23}^{1/2}}{k_6[I_2]^{1/2}}$$

K_{23} is well known from spectroscopic data and transition state theory may be used to calculate k_4/k_6. It is found that

$$\frac{k_4}{k_6} \approx \frac{E_6 - E_4}{RT}.$$

$E_6 - E_4$ probably lies between 4 and 8 kcal./mole, and on this basis R can be calculated for various temperatures and I_2 pressures. As is to be expected the importance of the chain mechanism increases with temperature and decreasing (I_2). At 600°K and $[I_2] < 400$ mm. the chain reaction contributes to the extent of about 10 per cent. Even at 800°K it does not completely replace the bimolecular process. This is in accordance with the change in the bimolecular rate constant found by Bodenstein. It does not explain the effect of surface which was found; this may be attributable to a third mechanism, or it is possible that the agreement with the suggested chain process is fortuitous and the whole of the deviations may be the result of a heterogeneous reaction. Further experimental work is undoubtedly required.

There are very few examples of termolecular reactions, the recombination of atoms and reactions involving NO being the only ones clearly established. The recombination of two iodine atoms in the presence of a third body has been intensively studied in a number of laboratories during the last few years and had been shown to follow the third order law quite accurately although the agreement in rate constants obtained in the several laboratories was not within the estimated errors of the methods used. These differences have now been shown to be caused partly by thermal effects and partly

by the fact that the influence of the relatively small amount of I_2 present had been ignored. It is found however [Christie *et al.* (7)] that I_2 is a very efficient third body for the transfer to energy from the association complex of two iodine atoms, being more than two-hundred times as efficient as argon or nitrogen.

The classical reaction between nitric oxide and oxygen has been reinvestigated in the pressure region 1 to 20 mm. by Treacy & Daniels (8) the reactions being followed optically. At higher pressures, the third order law was found to be accurately obeyed but at lower pressures the experimental law was

$$\frac{d[NO_2]}{dt} = k[NO]^{2\cdot2}[O_2]^{1\cdot0}.$$

Addition of NO_2 had a small inhibiting effect on the reaction. To explain these results the authors propose the following mechanism:

$$NO + O_2 \rightleftharpoons NO_3,\ K_A$$

$$NO_3 + NO \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NO_3NO$$

$$NO_3NO + NO_2 \xrightarrow{k_3} 2NO + O_2 + NO_2$$

$$NO_3 + NO \xrightarrow{k_5} 2NO_2$$

$$NO_3NO + NO \xrightarrow{k_6} 2NO_2 + NO$$

k_3 is included to explain the decrease in rate when NO_2 is added. If this rate constant is small we find

$$\frac{d[NO_2]}{dt} = [NO]^2[O_2]k_5K_A(1 + k_6k_1[NO]/k_5(K_2 + k_3[NO_2] + k_6[NO])$$

which is in agreement with the "greater than second order" behaviour of rate with NO and all the other observations.

In none of the above cases is the accepted theory of the mechanism shown to be wrong but merely incomplete. They do however serve as a warning of the difficulties to be expected in interpreting mechanisms in reactions of greater complexity and the danger of accepting too readily that the mechanisms have been well enough established to make small differences in apparent rate constants theoretically significant.

The importance of obtaining more information on the excited states of molecules and of energy transfer has been mentioned, and it is therefore encouraging to find that increasing attention is being paid to this problem, and that considerable progress is being made. The chemical kinetics of the excited state is the subject of a monograph by Laidler (9). In addition to a consideration of the production of excited states in radiation chemical reactions and a very brief (four pages) account of photochemical activation (the brevity being a result of the paucity of our knowledge of the subject) the monograph deals fairly fully with the reactions of excited species in flames and other high temperature systems.

At lower temperatures the transfer between translational and vibrational energy becomes of prime importance but the higher electronic levels—even if not significantly populated—may still nevertheless be of importance in determining the course of activation. Thus Szwarc (10) has pointed out that there is a close correlation between the "methyl affinities" of aromatic hydrocarbons and the energy difference between the ground state and the first excited triplet level. Although it must be admitted that in comparisons of this kind, correlations often exist between reactivity and a great number of physical properties of the molecule the correlation is in this case extremely good, and furthermore it seems reasonable that in passing towards the transition state the molecule should begin by approaching the potential energy surface of the triplet level thus passing towards a state with unpaired spins.

The triplet state is undoubtedly of importance as an intermediate in a wide variety of photochemical reactions in solution, and Porter & Wright (11) have now shown that it is also formed with comparable efficiency in the irradiation of aromatic molecules in the vapour phase. The nonradiative deactivation of the triplet state is more rapid in gases than in condensed systems but the lifetime (10^{-6} sec.) is still so much longer than that of the upper state first formed, that the triplet state can be expected to be of primary importance in the subsequent reactions of photoactivated molecules. Since these species are readily observed directly by their absorption an important new class of gas phase reactions becomes available for experimental investigation.

Quantitative knowledge of the elementary reactions of free atoms and radicals increases rapidly; the usual method of summarising the data in terms of a frequency factor and an activation energy seems to be entirely satisfactory at the present stage of experimental accuracy. An excellent monograph, devoted mainly to the elementary reactions of atoms and simple molecules in the gas phase, has recently appeared [Trotman & Dickenson (12)]. The author has concentrated mainly on reactions for which the mechanism seems to be well established, and as a result the work provides what is probably the clearest up-to-date account of elementary gaseous reactions.

It becomes increasingly difficult to do justice to the great quantity of published work in a review of this kind. In the sections to follow, much could be omitted for the good reason that it is covered by other chapters of this volume. Much has been omitted with no other justification than lack of space or that it was not entirely relevant to main themes chosen for discussion. Particularly regrettable is the omission of much other work published during the year because of lack of availability or of translation except in abstract; this applies particularly to work by Russian and Japanese authors.

Experimental Techniques

Much attention is being devoted to methods of studying the intermediates in a chemical reaction by direct observation, and future progress in the interpretation of complex reactions or even the energetic details of simple

reactions will probably be largely dependent on advances in such techniques.

For this purpose the mass spectrometer is proving particularly valuable, and its applications to reaction kinetics and other chemical problems have been reviewed by Dunning (13). Farmer & Lossing (14) have continued their study of the ionisation potentials of free radicals and have studied ethyl, isopropyl, and propargyl prepared by thermal decomposition. Because of the low concentration of free radicals in photochemical systems it has not previously been possible to detect them mass spectrometrically, but if advantage is taken of the high absorption coefficient of mercury for its own resonance radiation as much as 80 per cent decomposition of substances such as acetone may be achieved by mercury photosensitised reaction in times as short as two milliseconds, and the primary products—methyl and acetyl in this case—are readily estimated [Farmer *et al.* (15)]. An interesting type of gaseous reaction which could hardly be studied in any other way than mass spectrometrically is that between ions and molecules, e.g.

$$D_2^+ + D_2 \rightarrow D_3^+ + D$$

and

$$CD_4^+ + CD_4 \rightarrow CD_5^+ + CD_3$$

The rates of these reactions have been studied by Stevenson & Schissler (16) and are found to be independent of temperature and to correspond to nearly unit collision efficiency.

A second approach which is receiving much attention and has great potentialities is the trapping of labile products of a reaction in a solid matrix at low temperatures so that diffusion (and hence recombination) and also reaction with the matrix are inhibited. Whilst the products are examined in the condensed phase, the application of the information obtained to reactions in the gas phase is obvious. The labile species may be produced in the gas phase—e.g. by thermal decomposition—and then trapped by directing the gases onto a cold surface. In this way Rice & Scherber (17) have studied the products of thermal decomposition of hydrazine and have shown that the metastable yellow product which is formed is not paramagnetic and is therefore probably tetrazane. Dows, *et al.* (18) have studied the primary products of glow discharge decomposition of hydrazoic acid by infrared investigation of the condensed solid at 90°K, following Rice & Freamo (19) who reported the paramagnetic blue solid obtained under these conditions. They found, in addition to HN_3, NH_4N_3, and NH_3, infrared spectra of two other species which are thought to be N_2H_2 and $(NH)_x$ where x is unknown. The imine radical was not detected but its presence was inferred from the products. Broida & Pellam (20) used the same method to investigate the products of an electrical discharge through oxygen, liquid helium being used as refrigerant. Solid ozone was formed, and if water vapour was present they found evidence that their condensate contained free oxygen atoms.

Alternatively, the free radicals may be prepared *in situ* by irradiation of a solid solution and this has the advantage of giving a homogeneous trans-

parent system. Porter & Norman (21) have given details of their work on the preparation of solutions of free radicals in rigid glasses by photochemical dissociation, following the work of Lewis and his school (22). They show that the method is one of general applicability for the study of photo- or radiation chemical primary processes and the physical properties of free radicals and describe a number of new free radical spectra. As examples of use of the method for radiation chemical reactions Matheson & Smaller (23) have studied the species trapped in ice and other solids after γ irradiation at low temperatures. Using paramagnetic resonance methods they identified H, OH, and probably NH_2 in this manner.

Paramagnetic resonance absorption is particularly valuable in this kind of work and the detection of trapped radicals in a variety of systems has been possible. [See Ingram & Tapley (24), also Bamford *et al.* (25).] The application of paramagnetic resonance to fast reactions of free radicals in the gas phase does not seem to have been solved but holds considerable promise.

A modification of the flash photolysis technique which uses a Mg. spark in place of a gaseous discharge has been described by Mains, Roebber & Rollefson (26). The spark has the advantage of being practically monochromatic at 2800 A, though this is achieved only with a great loss in total intensity. Laporte (27) has given further details of his work on the study of fast reactions by kinematic spectrography. An interesting spectroscopic method of detecting oxygen atoms previously described by Gaydon (28) involves the observation of the luminescence of NO_2 accompanying the reaction between O atoms and NO. James & Sugden (29) have studied the luminescence in more detail and confirmed its origin by showing that its intensity is directly proportional to the product of the concentrations of O and NO. The reaction was studied in flames and the concentration of O atoms was calculated assuming equilibrium conditions.

For the study of the details of collisional processes the simplicity of molecular beams has always been attractive in spite of the experimental difficulties. Taylor & Datz (30) have described an interesting experiment in which a molecular beam of K atoms is crossed with one of HBr molecules, the profile of the product KBr being studied by surface ionisation gauges. Since the temperature of the two reactants and also their direction of approach can be varied separately, the method has many possibilities.

Further details of two methods involving measurement of the temperature profile in a reacting system have appeared [Kistiakowsky & Williams (31), also Callear & Robb (32, 33)]. The theory of the sodium diffusion flame method has been considered by Reed & Rabinowitch (34) who give a further treatment of the differential equations of continuity and show that the true rate constants are lower and the true activation energies somewhat higher (about 1 kcal) than those calculated in the usual manner.

In more conventional gas kinetic work the experimental problems are mainly analytical and the rapid developments in gas phase chromatography are very encouraging [See Littlewood, Philips & Price (35) and review of applications to gas kinetics by Callear & Cvetanovic (36)].

Theoretical

Whilst the calculation of frequency factors, both by collisional and transition state theories, does give a reasonably satisfactory account of experimental data, the absolute calculation of activation energies can hardly be considered feasible at present. The semi-empirical approach has never been very satisfactory, and recent applications of the method are no more encouraging.

Polanyi (37) has used the method in a way which might almost be called giving it its last chance. He has considered the eight reactions

$$CH_3 + HD, H_2, DH, D_2$$

$$CD_3 + HD, H_2, DH, D_2$$

for which experimental data are now available, mainly from Steacie's laboratory. One of the reactions is used to "calibrate" the potential energy surfaces, and these are then used to find the zero point energies in the initial and transition states. To get the best fit with experiment the proportion of coulombic energy to be used turns out to be that which gives the lowest barrier height consistent with no P.E. basin (7 per cent). The critical dependence on the proportion of coulombic energy chosen is again the objectionable feature of the method, and the author concludes that it is unlikely that the method could ever be used for the quantitative prediction of varying activation energies.

There have been several attempts to modify the method. Sato (38) has suggested a modified form of the London equation which, when used to calculate the surface for the reaction $H+H_2$, no longer gives a basin and double saddle point in the reaction path. Bigeleisen & Wolfsberg (39) have applied their semi-empirical method previously described (40) to the reactions $Cl+H_2$ and $Cl+HT$ and find good agreement with the data of Jones (41). Vogelaere & Boudart (42) have considered the transmission coefficient by carrying out classical calculations on the motion of a mass point on the P.E. surface corresponding to reactions of the type $AB+A \rightarrow A+BA$ and show that decrease of the transmission coefficient below unity would probably only be important in reactions of "hot" atoms or at high temperatures, e.g. flame reactions. Yasumori (43) has described a modified bond eigenfunction method of calculating P.E. surfaces and applied it to the $H+H_2$ reaction.

In a series of papers, Griffing and her collaborators (44, 45) have developed a molecular orbital theory of the activation energy in reactions between atoms and molecules and applied it to the reaction $H+H_2$ in particular. Correlation diagrams are constructed between the M.O.'s of the transition state and those of the reactants and products. This is an interesting approach which, even if not quantitatively satisfactory may prove useful, as similar orbital correlations have done in other fields. The method indicates the importance of low lying excited states of the interacting species in determining the activation energy, a factor which has little or no place in most other theoretical calculations of this quantity.

Another approach to the calculation of rate constants has been indicated by Coulson (46). He shows that the "methyl affinities" introduced by Levy & Szwarc (47) to describe the relative rates of addition of methyl radicals to aromatic molecules bear a close relation to the so-called localisation energy Ea (which is the loss in resonance energy due to substitution) and the free valence F. If r is the methyl affinity/effective atom referred to benzene $=1$, it is found empirically that

$$\log_{10} r = 16.66 - 6.57Ea = 29.44F - 2.40$$

The expression describes the data surprisingly well and could probably be used to predict other rates of methyl radical addition.

On the collisional theory of reaction rates the primary criterion of reaction is a collision between the reacting species such that the relative energy in the direction along the line of centres exceeds some critical value E^*. The number of such collisions, and hence the rate, depends on the number, S, of classical oscillators contributing to the energy. Pritchard (48) has calculated the rate constants for integral values of S for three hypothetical cases of $E^* = 5$, 10, and 20 kcal/mole. The Arrhenius plots given by these data are slightly curved such that for $S = 0$ the apparent activation energy increases with T and for $S \geqslant 1$ it decreases with T. Even for $S = 10$ the curvature would hardly be detected experimentally. In the particular cases of $Cl + CH_4$ and $Br + CH_4$ at least three oscillators would contribute, and Pritchard concludes that it seems possible that the rates of many, if not all, bimolecular reactions may be controlled by the ease of transfer of energy from the internal modes of vibration.

The first order rate constants of isotopic exchange reactions have been discussed in two papers. Bunton, Craig & Halevi (49) show that under most conditions likely to be realised in practice no deviation from first order kinetics should be observed as a result of isotopic fractionation or the mechanism of exchange except in cases involving deuterium. Marcus (50) has described a method of relating the first order rate constants to the individual steps of the process.

Tobin (51) has shown how the integrated kinetic expressions for a number of complex reactions involving second order steps may be recast to give a function of a concentration variable which is a linear function of time. The method should be useful for reducing fragmentary data when the experimental curves are sigmoid in shape, e.g. in autocatalytic oxidation.

Energy Transfer

The conversion of translational into vibrational energy, and its converse, are of fundamental importance in the production of the activated state, and since about 1930 a number of investigators have used acoustic interferometers to measure the rates of vibrational activation in diatomic and triatomic molecules. More recently improvements in electronic circuits have made possible similar measurements in polyatomic molecules which have very

short relaxation times. During the current year particular attention has been devoted to the halogen substituted aliphatic compounds.

Fogg & Lambert (52) have reported ultrasonic dispersion data for nine haloethylene compounds and have discussed their results in conjunction with similar data on halomethanes and other polyatomic molecules. The previously stated conclusion [Fogg, Hanks & Lambert (53)] that vibrational energy always enters a molecule via the mode of lowest vibrational frequency is supported by the recent work which also shows that the probability of excitation of this mode is a function, not only of its frequency, but also of its infrared activity. Polyatomic molecules possessing no internal rotation seem to fall into two classes described by the relations

$$Z_{10} = e^{0.0084\ \nu_{min}} \quad \text{Class I}$$

$$Z_{10} = e^{0.0175\ \nu_{min}} \quad \text{Class II}$$

where Z_{10} is the number of intermolecular collisions necessary for the molecule to lose one quantum of vibration and ν_{min} is its lowest vibration frequency. With certain exceptions, molecules whose lowest vibrational mode is infrared active fall into Class I and the others into Class II. It therefore appears that the polar properties which determine the intensity in the infrared are also fundamental in determining the ease of excitation of a vibration in a collision, a view put forward by McGrath & Ubbelohde (54) to account for the high efficiency of excitation of the 810 cm.$^{-1}$ vibration of ethylene by water vapour. In spite of this it seems that the energy always enters the molecule via the mode of lowest frequency whether this is infrared active or not.

Other workers have also confirmed that in general polyatomic molecules have a single relaxation time. Rossing & Legvold (55) have studied fourteen halogen-substituted methanes and confirmed that binary collisions are responsible for the excitation of vibrations. Their interpretation of the probability of excitation is different, however: they suggest that the probability depends on the relative energy of approach (rather than the relative velocity predicted by the Landau-Teller theory). Sette, Busala & Hubbard (56) have obtained some excellent experimental data on four substituted methanes—methyl chloride, methylene chloride, chloroform, and carbon tetrachloride. In contrast to other workers, they find that methylene chloride has two relaxation times, and this appears to be quite real and to result from better experimental techniques. The other three compounds have a single relaxation time.

There seems to be little doubt that in general only one vibrational mode is excited by collisions and that this energy passes very readily into other modes—i.e. the intermodal coupling is very strong.

Additional evidence has been obtained supporting the contention of Ubbelohde, based on viscosity and other data, that many hydrocarbons, in the gas phase, assume a "crumpled" configuration. Lambert and co-workers (57) have measured the viscosity and thermal conductivity of a large number of

hydrocarbons. They find that the ratio k/η is systematically lower for highly flexible molecules and suggest that this is due to some intercoiling of the molecules during a collision [cf. McGrath & Ubbelohde (54) also Peard, Stubbs & Hinshelwood (58)]. The mass diffusion coefficients of C_6-C_9 hydrocarbons in nitrogen and hydrogen have been measured [Cummings, McLaughlin & Ubbelohde (59)], and it is found that the most rigid hydrocarbons have the largest cross sections. Use of the Lennard-Jones 12-6 potential gives the same trend as do calculations based on the rigid sphere model. The cross section of a hydrocarbon when in a collision with H_2 is found to be greater than when it is in collision with N_2 (the "hydrogen effect"), and this is attributed to a greater probability of inelastic collision (i.e., conversion of translational into vibrational energy) in collision with hydrogen, an effect previously noted by Small and Ubbelohde (149) who found H_2 very effective in stabilising the HO_2 complex. The effect can hardly be general since hydrogen is little more effective than helium in stabilising the association of two iodine atoms [Russell & Simons (60)] nor in the transfer of vibrational energy from β naphthylamine [Boudart & Dubois (61)].

The work on β naphthylamine depends on the discovery by Neporent (62) that the fluorescence efficiency in certain aromatic molecules is increased as a result of vibrational deactivation by collision. The study of fluorescence yield from such molecules therefore provides a convenient alternative method of studying vibrational energy transfer, and the fact that the molecule is in a higher electronic state is unlikely to affect the generality of the results, though one would like to know a little more about the details of the stabilisation process before pressing the interpretation of the results too far. The result of Neporent (63) that H_2 is no more effective than helium in transferring vibrational energy from β naphthylamine is confirmed by the similar efficiency obtained for D_2. It would appear that neither the vibrational nor the rotational modes of hydrogen play any significant part in the vibrational energy exchange.

The mechanism of dissociation by impacts of the second kind has been considered by Groth & Oldenberg (64) with special reference to the reaction

$$Kr^* + N_2 \rightarrow Kr + 2N.$$

They conclude that this reaction occurs by excitation of the nitrogen molecule to a repulsive electronic state followed by dissociation in the time of one vibration rather than by conversion of the electronic energy of the krypton atom into vibrational energy of the nitrogen molecule. In fact there seem to be strong arguments against the commonly accepted idea of a resonance transfer of electronic energy completely into vibrational energy in this type of collision.

The transfer of electronic energy from a molecule or atom is most conveniently studied by observation of fluorescence quenching. The transfer of electronic energy from naphthalene to acridine and other molecules in the vapour phase has been confirmed as a true collisional process rather than the

trivial process of reabsorption of fluorescence or the effect of transparent foreign gases [Terenin & Karyakin (65)]. The quenching of fluorescence of anthracene, 9-phenyl anthracene and 9,10-diphenyl anthracene in the vapour phase is effected with nearly unit collision efficiency by O_2 and NO whilst the gases CO_2, A, C_2H_4 and CCl_4 have no effect up to concentrations of 10^{-2} mole/litre [Stevens (66)]. It seems likely that the effect of the paramagnetic gases is a spin-orbit coupling perturbation, though this does not explain the comparable efficiency of self quenching, nor is there any clear evidence that paramagnetic gases increase the population of the triplet state.

The dependence of quenching cross sections on the relative velocity of the quenching molecule has been studied in an interesting manner by Hanson (67). The effect of wave length on the relative intensity of sodium D radiation emitted by photolysed NaI was investigated. It was therefore possible to calculate the excess kinetic energy of the products and hence the relative speed of the sodium atom with respect to the quenching molecule. The quenching cross section of HCl and CO_2 decreased with increasing relative velocity, and H_2O showed little quenching action.

Elementaty Reactions of Atoms and Radicals

Chlorine, hydrogen, and oxygen atoms.—The relative reactivities of organic compounds with respect to hydrogen abstraction by a number of radicals and by hydrogen atoms have frequently been investigated and attention is now being given to the analogous abstractions by chlorine atoms. Pritchard, Pyke & Trotman-Dickenson (68) have used the competitive reactions

$$Cl + RH \rightarrow HCl + R \quad k_1$$

$$Cl + H_2 \rightarrow HCl + H \quad k_2$$

to determine the ratio k_1/k_2 by measurement of the residual hydrogen and hydrocarbon after reaction has proceeded for a certain time. The value of k_2 being known, k_1 can therefore be found. The values of frequency factors A and activation energies E were as shown in Table I. The A factors are never significantly greater than the collision numbers and in all cases the steric factor is greater than 0.1, i.e., considerably greater than in the analogous reactions of methyl as would be expected on entropy grounds. Comparison with the activation energies of similar reactions is interesting:

	log A	*E*
$Cl+CH_4$	13.4	3.9
$H+CH_4$	12.5	9.0
CH_3+CH_4	11.5	14.3
$Br+CH_4$	13.9	18.3

It is often suggested that the stronger the bond formed the less is the activation energy. The first three of the above reactions have identical (within 1 kcal.) energies of the bonds formed and it is clear that thermo-

TABLE I

FREQUENCY FACTORS AND ACTIVATION ENERGIES FOR VARIOUS SUBSTANCES REACTING WITH ATOMIC CHLORINE

RH	$A \times 10^{-14}$ (mole.$^{-1}$ cc. sec.$^{-1}$)	*E*(cal/mole)
H_2	0.79	5500
CH_4	0.26	3850
CH_3Cl	0.57	3360
C_2H_6	1.20	1000
C_2H_5Cl	0.46	1490
$CH_2(CH_3)_2$	1.76	670
$CH(CH_3)_3$	1.96	860
$C(CH_3)_4$	1.23	700
cyclo-C_5H_{10}	2.96	580

chemistry alone cannot account for the magnitude of activation energies It seems probable, as suggested by the authors, that the higher electron affinity of the Cl atom results in a decreased repulsion energy during its approach to methane.

Chambers & Ubbelohde (69) have determined the relative rates of monochlorination of paraffins and argue that these will run parallel to the rates of the reaction

$$Cl + RH \rightarrow R + HCl$$

since this will be the rate determining step. Apart from this assumption, the method is less reliable than that of Pritchard, Pyke and Trotman-Dickenson since the notorious sensitivity of these reactions to impurities and surface conditions may influence the results. However the values show the same trend as was previously found in rates of oxidation though the effects of molecular structure are less pronounced.

Callear & Robb (32) have measured the rate constants of addition of hydrogen atoms to olefines using the method previously described [Callear & Robb (70)] and have compared their results with those obtained by the molybdenum oxide method [Melville & Robb (71)] and the photolysis of hydrogen sulphide [Darwent & Roberts (72)]. The collision efficiencies are summarised as follows:

	Melville and Robb	*Darwent and Roberts*	*Callear and Robb*
C_2H_4	8.3×10^{-4}	0.81×10^{-4}	2.4×10^{-4}
C_3H_6	1.4×10^{-4}	1.1×10^{-4}	5.1×10^{-4}

Callear & Robb (33) have used the same method to study the reaction between H atoms and oxygen and they find that, at room temperature and low oxygen concentrations, a chain reaction occurs. They propose as chain steps

$$H + O_2 \rightarrow HO_2$$

$$H + HO_2 \rightarrow 2OH$$

$$OH + H_2 \rightarrow H_2O + H$$

Contrary to previous suggestions they find that the collision efficiencies of the first and second steps are very high and probably close to unity.

The reaction of H atoms with ozone results in the formation of OH radicals in excited vibrational levels ($v' = 9$) which can be detected by their emission spectra. The same reaction probably results in radiation observed in the night sky [McKinley, Garwin & Boudart (73)]. The recombination reaction

$$H + C_2H_5 \rightarrow C_2H_6$$

has been found to occur in the Hg-photosensitised hydrogenation of ethylene at room temperature and probably accounts for discrepancies in earlier work on this reaction [Smith *et al.* (74)].

The reaction of oxygen atoms, produced by the Hg photosensitised decomposition of N_2O, with ethylene has been studied [Cvetanovic (75)]. The activation energy for the first step of addition is estimated to be 3 kcal.

Methyl radicals.—More data are now available on the metathetical reactions of methyl than on any other class of elementary reaction. The methyl radicals are prepared by photochemical decompositions of acetone, acetaldehyde, azomethane, mercury dimethyl, etc. or by thermal decomposition of these and similar compounds. The agreement between absolute rate constants obtained by various methods is very satisfactory.

The reaction of methyl with nitric oxide, which is probably the commonest reaction involved in the inhibition of the thermal decomposition of hydrocarbons by this gas, has always been rather a mystery since the fate of the NO has not been established. Two investigations of this reaction by mass spectrometry have gone a long way towards answering the problem. Pretorius, Henderson & Danby (76) used methyl radicals from the photolysis of acetaldehyde and found that the rates of consumption of acetone and of nitric oxide were equivalent and no ethane was formed. Clearly the formyl radical does not react permanently with NO. They believe that the nitric oxide forms formaldoxine

$$CH_3NO \rightarrow CH_2{:}NOH$$

which polymerises, probably to a trimer, and decomposes at higher temperatures to HCN and H_2O. Bryce & Ingold (77) produced methyl by thermal decomposition of $Hg(CH_3)_2$ and fed the products of its reaction with NO directly into the mass spectrograph. With a residence time in the furnace of 5×10^{-2} sec. the products were NH_3, H_2O, HCN, CO, N_2, CO_2, CH_3CN and a peak at mass 45 (CH_3NO?) in addition to products of thermal decomposition of $Hg(CH_3)_2$. With shorter residence times only CH_3NO was detected. Their results indicate zero activation energy for the combination $CH_3 + NO$ and a rate constant of 1.3×10^{11} cc. mole^{-1} sec.$^{-1}$. Although the secondary de-

composition products are complex, the inhibition reaction itself seems therefore to be quite straightforward.

Further metathetical reactions of methyl with hydrocarbons have been studied. Rice & Varnerin (78) have studied relative rates by isotopic methods and confirmed the low value (6.3 kcal.) for the activation energy of reaction with acetone. Varnerin (79) has established that reactions of the type

$$CD_3 + C_2H_6 \rightarrow CD_3CH_3 + CH_3$$

occur to the extent of one in 1500, 2500, and 90, compared with H abstraction in C_2H_6, CH_3OCH_3, and CH_3COCH_3 respectively, but to the extent of 10 per cent in propylene. Dainton & McElcheran (80) have found the rate constant for hydrogen abstraction from acetone

$$k = 5.8 \times 10^8 \, e^{-9.8/RT} \text{ 1/mole/sec.}$$

in excellent agreement with previous work and have studied the reaction $CH_3+CD_4 \rightarrow CH_3D+CD_3$ for which they find

$$k = 1.8 \times 10^8 \, e^{-12.9 \pm 0.65/RT} \text{ 1/mole/sec.}$$

Wijnen (81) finds the activation energy for hydrogen abstraction from ethane by CH_3 to be 11.2 ± 0.3 kcal./mole (cf. value of 10.4 of Trotman-Dickenson Birchard & Steacie (150). The hydrogen abstraction from acetaldehyde has been studied by Ausloos & Steacie (82) and by Dodd (83) and the lower value of activation energy again confirmed. Ausloos & Steacie have shown that only the acyl hydrogen is captured and find $E=6.8$ for CH_3CHO, and $E=7.8$ for CH_3CDO. Dodd studied the reaction by the most reliable method —which has not previously been possible—the measurement of ethane formed. For the rate constant he finds

$$k = 10^{10.8} \, T^{1/2} \, e^{-8000/RT} \text{ mole}^{-1}\text{cm.}^3\text{sec.}^{-1}$$

These lower values of activation energy lead to a much more reasonable value of the frequency factor. The higher values previously found probably arose from the fact that the acetaldehyde photolysis is undoubtedly complex, the complications perhaps being caused by other reactions which affect the relation between CH_3 concentration and light intensity.

Oswin, Rebbert & Steacie (84) find the activation energies for hydrogen abstraction from $(CH_3)_2Hg$ are 10.0 and 10.2 kcal./mole for CD_3 and CH_3 respectively and since, in the former case, CD_3CH_3 was found in the products it seems that the reaction

$$CD_3 + (CH_3)_2Hg \rightarrow CD_3CH_3 + Hg + CH_3$$

is significant in accordance with earlier observations that the quantum yield of the reaction can exceed unity.

Hydrogen abstraction by methyl from HBr proceeds very readily, as little as 1.5 mm. HBr in 50 mm. acetone completely eliminates ethane formation at 150°C. [Ridge & Steacie (85)]. The acetyl radical also reacts readily, and failure to allow for these reactions invalidates earlier work

on reactions between methyl radicals and haloethanes which are very complex [Ridge & Steacie (86)]. Although acetone photolysis is the best established source of methyl radicals, even here there are slight complications as evidenced by curvature in the Arrhenius plots of $RCH_4/R^{1/2}C_2H_6$. One reaction which contributes to these effects found by Ausloos and Steacie (87) is $CH_3+CH_3CO \rightarrow CH_2CO+CH_4$.

Other radicals.—Gray (88) has reviewed the reactions between alkyl radicals and NO_2. There are three types of reaction leading to the formation of nitroparaffins, alkyl nitrites, and a split to alkoxy radicals and nitric oxide respectively, the incidence of each being dependent mainly on the relative energetics of the processes. Gray gives a useful table of standard enthalpies of formation of alkyl and alkoxy radicals, nitroalkanes, and alkyl nitrites.

The reactions of CF_3 radicals from the photolysis of hexafluoracetone have been studied by Aysgough, Polanyi & Steacie (89). CF_3 abstracts hydrogen from CH_4 and C_2H_6 more readily than does CH_3, the activation energies being respectively 10.3 ± 0.5 and 7.5 ± 0.5 kcal./mole. The steric factors seem to be normal. The photolysis is a clean source of CF_3 radicals, the only products being CO and C_2F_6 in equal amounts.

The abstraction of hydrogen from H_2 by propyl is accompanied by an activation energy of 12.5 kcal. (1.2 kcal. greater than the analogous reaction of ethyl). The ratio of disproportionation to recombination of propyl radicals is 0.5 at room temperature [Hoey & Le Roy (90)]. Propyl radicals may react in three ways in the presence of oxygen

$$C_3H_7 + O_2 \xrightarrow{1} C_3H_7OO \rightarrow \text{oxygenated organic products}$$

$$C_3H_7 + O_2 \xrightarrow{2} C_3H_6 + HO_2$$

$$C_3H_7 \xrightarrow{3} C_2H_4 + CH_3$$

E_2-E_1 has the value 19 kcal. and $P_2/P_1=4\times10^6$ [Satterfield & Reid (91)].

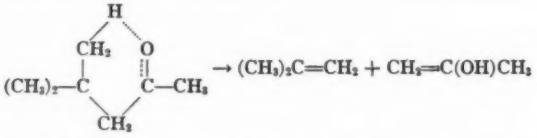
The reaction between two different alkyl radicals has been studied by Ausloos & Steacie (92) using the photolysis of methyl ethyl ketone. The ratio of disproportionation to recombination rates of methyl and ethyl is found to be 0.04 and the activation energies of both reactions are nearly zero.

Photochemistry

There is no satisfactory theory of the primary processes of photochemical decomposition nor indeed of the analogous processes occurring during thermal decomposition, nor are there sufficient experimental data available on primary processes in polyatomic molecules to make it clear how closely one follows the other. If a single bond is broken it is usually found to be the weakest in the molecule, but fission into two molecules also frequently occurs.

In the final approximation the probabilities of such processes depend on the detailed shape of the potential energy surfaces of the excited molecules and there is little hope of being able to calculate these with sufficient accuracy at present. Even for a more empirical approach many more experimental data are required and only in the case of aldehydes and ketones is there a sufficient body of evidence to reveal any general principles. A detailed knowledge of primary processes in aldehydes and ketones is doubly important in view of the value of these substances in the study of free radical reactions.

Martin & Pitts (93) have discussed the primary processes of photodecomposition in ketones along with new data on methyl neopentyl ketone. It is becoming clear that all aliphatic ketones undergo fission into free radicals to some extent and that complex ketones having alkyl groups with hydrogen in the γ position dissociate also by the Norrish type II mechanism [Norrish (94)] into an olefin and a lower ketone. It is likely that this reaction proceeds via a six-membered cyclic transition state and the enolic form of the ketone [Davis and Noyes (95)]; e.g.



The following table of quantum yields, ϕ, has been compounded by Martin & Pitts:

TABLE II

QUANTUM YIELDS

	ϕ (rearrangement)	ϕ CO
CH_3COCH_3	0.0	1.0
$CH_3COC_2H_5$	0.0	0.84
$CH_3CO(CH_2)_3CH_3$	0.48	0.11
$CH_3COOH_2CH(CH_3)_2$	0.35	0.15
$CH_3COCH_2C(CH_3)_3$	0.23	0.04

It shows clearly that a γ hydrogen is required for rearrangement reactions and also indicates that the reaction occurs more readily when this is a secondary hydrogen,—as would be expected.

In accordance with these ideas Whiteway & Masson (96) have found that the photolysis of diisopropyl ketone is entirely a free radical process with a quantum yield of CO production of unity, whilst with di-*n*-propyl ketone 40 per cent goes to ethylene and methyl-*n*-propyl ketone. It is worth noting that Nicholson (97) has pointed out that a study of cracking patterns of ketones in the mass spectrometer suggests that excitation by electron bombardment results in similar modes of decomposition.

The low quantum yield of acetone photolysis has been shown by Naldrett (98) to be attributable to the recombination of CH_3 and CH_3CO, the primary quantum yield being unity. The formyl radical has been detected spectroscopically in the products of flash photolysis of acetaldehyde, formaldehyde, biacetyl, propionaldehyde, acraldehyde, and methyl and ethyl formates [Herzberg & Ramsay (99)]. The ratio of molecular to radical split in acetaldehyde photolysis has been measured by means of NO inhibition by Pretorius, Henderson & Danby (76)].

The primary processes in the photolysis of acetic acid have been studied by Ausloos & Steacie (100) using CH_3COOD. The molecular split to CH_3D and CO_2 occurs to the extent of 10 per cent and is accompanied by at least three modes of decomposition into radicals. The photolysis of acetaldazine $CH_3CH{=}N{-}N{=}CHCH_3$ was studied as a possible source of the ethylidine radical by Brinton (101), but there appear to be several primary mechanisms and the products are complex. Similarly, Noyes & Rohr (102) who hoped to use nitrogen dioxide as a source of oxygen atoms and to study the reaction of these with hydrocarbons, found the reaction too complex to be useful for this purpose. On the other hand the photolysis of hexafluoroazomethane is straightforward and a useful source of CF_3 radicals [Dacey & Young (103)].

In the fifty-first paper of the series Sheats & Noyes (104) report a detailed study of the photolysis of biacetyl with particular reference to its fluorescence. The decomposition has also been studied by Ausloos & Steacie (105). Although these results are in agreement with the earlier work of Blacet and Bell, the mechanism is again complex and shows a marked dependence on wavelength. The photooxidation of azomethane at low O_2 pressures has been studied by Hoey & Kutschke (106) who find that the reaction between CH_3 and O_2 has a very small activation energy and a steric factor of 10^{-2}.

The photochemistry of aromatic vapours has received remarkably little attention in the past because of various experimental difficulties, particularly of analysis. These molecules would nevertheless seem to provide the best system of all for the study of primary photochemical processes, especially since they show a number of interesting phenomena (e.g., phosphorescence) not normally encountered in the aliphatic series. Porter & Wright (107), in a preliminary study of the absorption spectra of the primary dissociation products of a number of aromatic vapours, have found that the only cases where free radical products are observed are those in which the radical formed has a resonance stabilised semiquinone type structure. The absorption spectra of benzyl, anilino, phenoxy, and similar free radicals are described, and the observations suggest that their collisional efficiency of recombination is at least 10^{-1} to 10^{-2}.

Mercury-photosensitised decompositions provide an important source of radicals and atoms and a number of applications of the method have already been mentioned. Cvetanovic (108) has studied the quenching of mercury resonance radiation both to the metastable $^3P_0$ level, and to the

ground state, by hydrocarbons. The reaction of Hg^3P_1 with toluene seems to result in two decomposition processes, one to benzyl and a hydrogen atom and the other to phenyl and methyl [Sehon & Darwent (109)], and there is also evidence that two different excited states of toluene are involved. There also appear to be two separate primary steps in the Hg photosensitised decomposition of ethylene oxide [Cvetanovic (110)].

The presence or absence of hydrazine in the products of the mercury-photosensitised decomposition of ammonia has been shown by McDonald & Gunning (111) to be a question of whether the hydrazine is allowed to react further. It is rapidly removed by reaction with the H atoms produced from ammonia. Yields of hydrazine as high as 95 per cent have been obtained in flow systems at high flow rate, whilst in static systems the products are exclusively N_2 and H_2. The question whether the formation of acetylene in the Hg photosensitive decomposition of ethylene is an intramolecular or a free radical process has been studied by Cvetanovic & Callear (112). Since the products formed from a mixture of normal and deuterated ethylenes are almost exclusively H_2, D_2, C_2H_2, and C_2D_2, it seems to be quite definitely intramolecular.

Reactions of Active Nitrogen

The true nature of the reactive species in active nitrogen is still obscure, although there seems to be no doubt that nitrogen atoms are important. The effect of a magnetic field shows that ions play some part in the short afterglow [Kane & Clark (113)], but the chemical reactivity is attributable to a neutral form of nitrogen [Varney (114)]. There is also evidence that excited molecular nitrogen is not important [Freeman & Winkler (115)]. Positive evidence comes from the observation of infrared N_1 lines in the negative glow [Stewart & Emeleus (116)]. On the other hand, Freeman & Winkler (117) believe that there must be two active species to account for results on the decomposition of ammonia, and Kentz (118) believes three such species are necessary to explain his observations on the excitation of metal vapours by active nitrogen. The activation energies and steric factors for the reactions between active nitrogen and a number of hydrocarbons are given by Onyszchuk & Winkler (119), and the reaction with azomethane has been studied by Armstrong & Winkler (120).

Thermal Decomposition

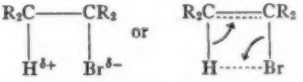
Maccoll and collaborators have described an extensive investigation of the mechanisms and rates of pyrolysis of organic bromides. The reaction in all cases results in the elimination of HBr, and it is found that this may result from a C—Br bond fission followed by chain reaction, as happens with *n*-propyl bromide [Agius and Maccoll (121)], or a similar break but without ensuing chains, as happens with allyl bromide [Maccoll (122)], or a straight unimolecular split directly into the molecular products as seems to happen in most other cases. Frequency factors, A, and activation energies, E, for reactions of the latter type are shown in Table III.

TABLE III

FREQUENCY FACTORS AND ACTIVATION ENERGIES FOR UNIMOLECULAR SPLIT OF ORGANIC BROMIDES

	A (sec^{-1})	E (kcal./mole)	Reference
isopropyl	4.17×10^{13}	47,800	Maccoll & Thomas (123)
sec butyl	4.27×10^{12}	43,800	Maccoll & Thomas (124)
tert. butyl	1.0×10^{14}	42,000	Harden & Maccoll (125)
cyclohexyl	3.24×10^{13}	46,100	Green & Maccoll (126)

The relative rates and activation energies of the unimolecular split into molecular products are discussed, along with unpublished data on other similar reactions by Maccoll & Thomas (127). They show that there is no correlation with the homolytic bond dissociation energy of the C—Br bond but rather a good correlation with the heterolytic bond dissociation energy $D(R^+Br^-)$. They suggest that there is an analogy between reactions in the gas phase and in polar solvents the transition state being represented by



The important findings of Hinshelwood and collaborators on the specific effects of foreign gases on thermal decomposition rates have already been mentioned. It will not be possible to do more than list briefly a few of the other investigations of pyrolytic reactions.

The thermal decomposition of germane is a first order, homogeneous reaction at high pressures, but a zero order germanium surface reaction at low pressures (128, 129). A preliminary investigation of the pyrolysis of C^{14}-labelled ethane using the toluene carrier technique gives a value of 85 to 89 kcal. for the activation energy of dissociation and 7×10^{14} to 5×10^{15} for the frequency factor [Leigh, Szwarc & Bigeleisen (130)]. The decomposition of nitromethane at high pressures proceeds via two primary processes, one a fission to CH_3NO and O, the other to CH_3 and NO_2 [Mueller (131)]. Pyrolysis of mercury dimethyl leads to values for the dissociation energy of the first and second bonds of 51.3 and 5.5 kcal./mole [Long & Laurie (132)]. The formation of CH_3D by decomposition of hydrocarbons (*n*-butane) in the presence of D_2 has been shown to be no criterion of the participation of alkyl radicals in the NO-inhibited decomposition [Danby, Small, Stubbs & Hinshelwood (133)]. The residual reaction, inhibited by NO and propylene, in the H_2/D_2 exchange, unlike that in hydrocarbons, is heterogeneous, and, since this shows that NO inhibits H atom chains, the residual reaction in hydrocarbons cannot be of this type [Stephen & Danby (134)]. The reactions occurrying in the flame decomposition of ethyl nitrate [Needham & Powling (135)] and of methyl nitrate and nitrite [Gray, Hall & Wolfhard

(136)] have been described. The pyrolysis of ethyl bromide, on the basis of the work described at the beginning of this section, would be expected to be a radical chain reaction. Maccoll & Thomas (137) have challenged the unimolecular mechanism proposed by Friedman, Bernstein & Gunning (138) who now agree, on the basis of their recent work, that radical chains are involved. The thermal decomposition of nitroalkanes has been studied by Gray, Yoffe & Roselaar (139) who show that an intramolecular elimination of nitrous acid is not alone capable of explaining the results. In the pyrolysis of biacetyl the abstraction of hydrogen by methyl is about five times more rapid, at 436°C., than reaction to give acetone and acetyl [Guenther, Whiteman & Walters (140)]. The thermal decomposition of nitric oxide above 1400°K. is homogeneous and second order with an activation energy of 63.8 ± 0.6 kcal. [Kaufman and Kelso (141)].

Miscellaneous

A number of isotopic exchange reactions have been studied. The equilibrium constant of the exchange

$$^{14}CO + COCl_2 \rightleftharpoons CO + {}^{14}COCl_2$$

is independent of all factors except temperature, and the temperature dependence is adequately predicted by statistical mechanical methods [Stranks (142)]. The kinetics of the exchange in photochemical and thermal reactions have been very carefully studied by Stranks. The mechanisms are consistent with previous nontracer studies, and the large isotope effect which is observed arises from a multiplication of an equilibrium effect by a unidirectional one. The exchange of isotopic chlorine between HCl and the series CH_3Cl, CH_2FCl, CHF_2Cl, and CF_3Cl has been studied by Boggs & Brockway (143). There are remarkable differences between the various reactions in such matters as their dependence on surface/volume ratio, and the authors point out the danger of such statements as "introduction of fluorine into organic halides makes the halogen less reactive" without a detailed knowledge of mechanisms. The exchange between HF and F_2 is entirely heterogeneous [Adams, Bernstein & Katz (144)].

The reactions of N_2O with H_2, CO, and hydrocarbons have been previously studied, and in most cases radical chains are involved. In the reaction with SO_2 the reaction is simpler, the fission into N_2 and O being followed by simple addition to form SO_3 [Bell, Robinson & Trenwith (145)]. Further work on the addition of BF_3 to amines has been reported by Kistiakowsky & Williams (31). The rates of addition are all smaller than the rate of recombination of methyl radicals, and the reactions probably have a small activation energy. The reaction between nitric and nitrous oxides has been found by Kaufman & Kelso (146) to have an activation energy of 50 kcal. and a frequency factor of 2.5×10^{14} cc. mole^{-1} sec.$^{-1}$ which is more reasonable than earlier values. A preliminary report of a study of the reaction between hydrogen and nitrogen dioxide has been given by Ashmore & Levitt (147).

A recommendation, which any review writer would endorse, that reaction kinetic units be standardised, has been given in the *Journal of the American Chemical Society* (148). The units proposed are seconds, moles/litre and—for light intensity—einsteins. Presumably einstein/sec. is intended.

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COMBUSTION AND FLAMES[1]

By C. E. H. Bawn and C. F. H. Tipper

Department of Inorganic and Physical Chemistry, University of Liverpool, Liverpool, England

The voluminous amount of work in the field of combustion precludes a complete and general discussion of the subject, and in this short review topics have been selected which indicate the main trends of development during the last two years. No attempt is made to survey the very extensive work on technical problems of combustion or detonation phenomena. The reports of several meetings have been published, viz.: *Selected Combustion Problems* (*Fundamental and Aeronautical Applications*) (1), an AGARD Colloquium held at Cambridge, England, December, 1953; Fifth Symposium (International) on Combustion held at Pittsburgh, Pennsylvania, August–September, 1954 (101 papers) (2); *Combustion Researches and Reviews, 1955* (invited papers presented at the sixth and seventh AGARD Combustion Meetings held at Scheveningen, Holland, May, 1954 and at Paris, France, November, 1954) (3). Treatises published include *Physical Measurements in Gas Dynamics and Combustion* (Volume 9 of the *Series on High Speed Aerodynamics and Jet Propulsion*) (4), *Spontaneous Ignition of Liquid Fuels* by B. P. Mullins (5), and *Some Fundamentals of Combustion* (Gas Turbine Series, Volume 2) by D. B. Spalding (6).

Kinetics and Mechanism of Gaseous Combustion

The researches reported on the slow and rapid combustion of gaseous mixtures have been mainly directed towards the elucidation of the mechanism of combustion reactions and with few exceptions have been along accepted lines. This work is summarised under the following main headings: slow oxidation studies, cool flames, ignitions and ignition limits, and elementary reactions which occur in combustion systems.

Slow combustion.—The complete mechanism of the thermal H_2-O_2 reaction is still not settled. Patrick & Robb (7) concluded that the initiating reaction was heterogeneous and proposed a reaction scheme involving the poisoning by water of active centres on the surface normally responsible for the formation of hydrogen peroxide, the dissociation of which initiated the reaction. Anzilotti and co-workers (8) observed that the small amount of hydrogen peroxide found in the slow oxidation at 540°C. in a borosilicate glass vessel, was eliminated by a PbO coating. The addition of methane has been found to increase the initial rate of the H_2-O_2 reaction at 560°C. and either to increase or decrease the maximum rate according to the H_2/O_2 ratio (9). It was suggested that the methane undergoes reactions which in-

[1] The survey of literature pertaining to this review was completed in December, 1950.

crease the initial rate of water formation and that water acted as a homogeneous catalyst. The rate of the CO-O_2 reaction was increased by small additions of hydrogen and methane, but larger additions of the latter had a retarding effect (10). The slow combustion of methane in the temperature range 500–1000°C. has been investigated by several workers (11, 12, 13, 14). The oxidation of the CO formed occurred simultaneously and the two oxidations interacted with one another, as shown by the marked change in the kinetics with rise of temperature. The rate was more sensitive to oxygen pressure and much less sensitive to methane and total pressure as the temperature was increased and above 600°C. methane may even retard its own oxidation. The effect of surface on methane oxidation has been studied by Urizko & Polyakov (15) and extensively by Hoare & Walsh (14) who observed that the kinetics differed markedly according to whether the surface had been HF treated or aged, heat treated or coated with PbO. Vanpee & Grard (16) have examined the effect of formaldehyde on the oxidation of methane. During the induction period in the oxidation of ethane at 350°C., formaldehyde, acetaldehyde and peroxides are formed and their concentrations increase exponentially (17). Addition of CH_3CHO or Et_2O_2 shortened the induction period.

The formation of olefins and hydrogen peroxide during the slow combustion of higher hydrocarbons in the "high temperature" range (350° to 500°C.) is of considerable importance, as exemplified by work with propane (18 to 21). Satterfield & Reid (21) conclude that the propyl radical initially formed reacted in three ways:—

$< 300°C.$ $C_3H_7 + O_2 \rightarrow C_3H_7O_2 \rightarrow CH_2O$, CH_3CHO, CH_3OH, CO, CO_2, peroxides. 1.

$300°$ to $500°C.$ $C_3H_7 + O_2 \rightarrow C_3H_6 + HO_2$ 2.

$> 500°C.$ $C_3H_7 \rightarrow CH_3 + C_2H_4$ 3.

They have been able to correlate a mass of published data on the oxidation in a very satisfactory way and calculated $E_2 - E_1 = 19$ kcal. per mole and $P_2/P_1 = 4 \times 10^{-6}$. It seems that the anomalous effect of temperature on the oxidation of propane may be due to the partial replacement of reaction 1, by the nonbranching reaction 2.

The effect of temperature on the slow combustion of *n*-butane from 260° to 540°C. has been analysed by means of Semenov's relation for the exponential acceleration to the maximum rate (22) and the results are explained by postulating competing reactions of a relatively stable intermediate. A detailed study of the progressive accumulation of products and consumption of reactants in the oxidation of isobutane at 291°C. has been made by Ridge & co-workers (23, 24). The results supported the viewpoint that the termination of the induction period was due to the accumulation of an active intermediate, which was not peroxidic. The products of the oxidation of *n*-butane (25), 2,2-dimethylbutane (26), *n*-heptane (27, 28), 2,2,4-trimethylpentane (26, 27, 28) 2,2,5-trimethylhexane (27) and cyclohexane (29) have been ex-

plained by consideration of the various modes of reaction of radicals formed by the initial hydrogen abstraction from the hydrocarbon.

Recent work has brought out some differences between the slow combustion of olefins and that of paraffin hydrocarbons. Bawn & Skirrow (30) have summarised measurements with propylene, butene-2, and hexene-1. They found that excess olefin tended to retard the oxidation due to the formation of resonance stabilised radicals. 2,2,4-trimethylpentene-1 (diisobutylene) oxidised very slowly below about 450°C. (31), and its retarding effect on the oxidation of *n*-heptane, was ascribed to the reaction

$$RO_2 \text{ (from heptane)} + C_8H_{16} = ROOH + C_8H_{15} \text{ (inactive)}.$$

The reaction of benzene and phenol with oyxgen in the gas phase at 500° to 650°C. has been studied by Ioffe & co-workers (32, 33, 34). The pressure of an ether-oyxgen mixture at 160° to 175°C. (just below the cool flame limit) was observed to decrease at first and then rise (35). The pressure drop was eliminated by a KCl coating on the vessel walls. The kinetics of the slow combustion of *n*-ethyl, propyl, and butyl alcohols has been investigated by Newitt (36) and that of trimethylamine and triethylamine by Cullis & Waddington (37). The change of rate with length of the carbon chain of the alcohols was less than that with the corresponding hydrocarbons, although the kinetic relationship appeared to be similar. The mode of oxidation of trimethylamine seems to be very different from that of triethylamine and other amines.

There is continuing interest in the respective roles of peroxides and aldehydes in slow combustion in the "low-temperature" range (<350°C.). The difficulty of distinguishing hydrogen peroxide, aldehyde peroxides and alkyl hydroperoxides in the products has not been satisfactorily overcome (38 to 44). Various results (23, 24, 30) suggest that alkyl hydroperoxides first formed give aldehydes which may lead to chain branching.

The photo-oxidation of formaldehyde at 100°C. has been investigated by Style & co-workers (45, 46) and the thermal oxidation at 300° to 400°C. by Scheer (47). The products included peroxidic substances, probably HCO_3H and $(CH_2OH)_2O_2$ formed together with HCOOH during the thermal reaction in "aged" vessels. The first authors propose a reaction scheme involving H, HCO, HO_2 and two more complex chain carriers. Scheer found that in the presence of mercury vapour or freshly cleaned silica surfaces, no peroxides were formed and the rate commenced at its maximum value, whilst in an "aged" vessel

$$\frac{d(p)}{dt}_{\text{initial}} < \frac{d(p)}{dt}_{\text{max.}},$$

though the overall kinetics were the same. He suggested that HCO_3H was formed by a simple chain reaction and was then either destroyed at the walls or reacted with the formaldehyde to give $(CH_2OH)_2O_2$. A luminescent phenomenon observed during the combustion of a rich mixture of formaldehyde

and oxygen at temperatures around 500°C., by Vanpee (48) was said to be associated with the decomposition of intermediary peroxides. McDowell & Farmer (49) have discussed the mechanism of the oxidation of acetaldehyde and concluded that peracetic acid formed in the thermal reaction causes chain branching.

The rate of the pressure decrease which follows the induction period of the reaction between trimethylsilane and oxygen at 220° to 250°C. (50) has been found to correspond closely to the rate of oyxgen consumption. It was suggested that initiation was by oxygen attack on the Si-H bond and further oxidation formed groups, which condense to silicone oils.

Leger (51) has described a modified form of mass spectrometer for recording the variation in the concentration of substances during gas phase oxidation.

Cool flames.—The peculiar phenomena known as cool flames have excited interest for many years and continue to do so, though there is still no agreement on the reactions responsible for their propagation in a combustible mixture. Franze, Jost & Lesemann (52) have analysed the problem theoretically on the assumption that only diffusion processes are responsible for flame propagation. A blue pre-ignition glow observed with weak methane-air mixtures using a motored compression-ignition engine has been extensively studied by Gaydon, Moore & Simonson(53). Formaldehyde was formed and lean mixtures showed a yellow luminosity due to carbon particles. They suggested that methane possessed a cool flame region, possibly due to formation and breakdown of methyl hydroperoxide, and that some polymerisation may precede the appearance of the glow. Knox & Norrish (54, 55) have investigated the cool flames of ethane and propane. The products of the cool flames of propionaldehyde were shown to be similar to those of propane. With rich C_2H_6-O_2 mixtures up to three cool flames have been obtained. It was suggested that their origin was a side reaction indicative of higher aldehydic or peroxide derivatives. Multiple cool flames (up to five in number) in a butane-oxygen mixture have been observed at temperatures between 280°C. and 330°C., and although the part played by aldehydes and peroxides has been extensively studied by Bardwell (56), no definite conclusion was reached as to the intermediate responsible for the periodicity of the flames.

Neiman & co-workers have also investigated cool flame phenomena with propane (57), butane (58), butene-2 (59), and *n*-pentane (60) and the cool flame regions for *n*-pentane-oxygen mixtures have been studied as a function of pressure and composition at around 350°C. (61, 62). The results of a polarographic study of the peroxidic and aldehydic products from the cool flame oxidations of four isomers of hexane have been reported (63). The effect of various factors on the intensity and duration of cool flame luminescence with *n*-pentane, *n*-heptane, and 2,2,4-trimethylpentane-oxygen mixtures in a motored engine (64) has shown that the yield of carbonyl compounds, which included acrolein and crotonaldehyde, was proportional at any time to the integrated intensity of the cool flame up to that time.

Foresti (65) has been able to stablise the cool flame of diethyl ether (and of *n*-hexane and *n*-heptane) above a burner and a preliminary report of the temperature profiles and products indicated results of considerable interest.

Ignitions and ignition limits.—The effect of conditions on the limits and induction periods of spontaneous ignition of combustibles is a valuable method for the elucidation of the mechanism of the oxidation reaction. The minimum spontaneous ignition temperatures in air and their relation to molecular structure have been determined for a large number of substances (66).

The effect of added substances on the H_2-O_2 explosion continues to attract considerable interest. Sayasov (67) has analysed the problem of the third limit mathematically. From a discussion of the kinetics of the nonlinear chain reaction associated with water formation, he concluded that at pressures near 1 atm. the reaction $O+H_2+M=H_2O+M$ played an essential role in the oxidation. A PbO coating has been shown to raise the explosion temperatures of H_2-O_2 mixtures but addition of small amounts of SO_2 had no effect (68). Ashmore (69) has expanded earlier work (70, 71) on the sensitised H_2-O_2 ignition and has found that the lower and upper limits were substantially the same whether the additive was NOCl, NO_2, or NO_2+NO, in spite of very different induction periods. These induction periods were assumed to be the times for the additives to decompose to NO, and the proposed reaction chain mechanism involved excited NO molecules. The effect of hydrocarbons on the second explosion limit has been investigated in clean Pyrex and KCl coated vessels (72, 73, 74, 75). The raising of the limit by small amounts of methane or any concentration of ethane and propane was explained by reaction between hydrogen atoms and hydrocarbon molecules to give radicals which terminated the chain. At a certain critical concentration of methane the explosive reaction was completely inhibited, and this was ascribed to the formaldehyde produced (76). Second explosion limits of H_2-CO-O_2 mixtures have been studied by Dixon-Lewis (77). As CO replaced H_2 the limit was raised until the CO concentration reached 80–85 per cent, when it dropped sharply. The results indicated that the specific chain breaking effect of CO, apart from its effect as an "inert" gas, did not become appreciable until the amount of H_2 in the mixture became quite small. It was concluded that a bimolecular association reaction between CO and oxygen atoms was largely responsible for the observed "chemical" effect.

The influence of NO, NOCl, chloropicrin (CCl_3NO_2), and NCl_3 on the ignition of H_2-Cl_2 mixtures has been examined by Ashmore (78). Sensitisation was ascribed to the introduction of fresh chlorine atoms to the main chain and retardation to new termination reactions which removed chlorine atoms. The region of ignition with NCl_3 was shown to be closely connected with the region of explosive decomposition of NCl_3 vapour itself. Satterfield *et al.* (79) have investigated the limits of the explosive decomposition of hydrogen peroxide vapour and the effect of packing and addition of inert gas. The limits for the delayed ignition and explosive combustion of gaseous

hydrazine have been determined by Gray & Lee (80, 81). The explosion was inhibited by a KCl coating and facilitated by addition of nitrogen or argon. Delayed ignition at temperatures above 420°C. and at pressures lower than the explosion limit was ascribed to hydrogen produced by a side reaction. This accumulated until the hydrazine disappeared, when the H_2-O_2 mixture exploded.

The diborane-oxygen system has been studied by Whatley & Pease (82) and by Roth & Bauer (83). The former found that between 105°C. and 165°C explosion occurred after an induction period. They suggested that slow decomposition gave rise to a product which acted as a sensitising agent and that neither B_2H_6 nor BH_3 reacted directly with oxygen under the experimental conditions. However, Roth & Bauer, using a method in which appropriate mixtures were heated very rapidly to predetermined temperatures, were able to determine three inflammation limits, at temperatures between 150°C. and 200°C. and pressures below 50 mm. for which there was no induction period before explosion. They proposed a mechanism analogous to that of the H_2-O_2 reaction. Temperature-composition limits of spontaneous ignition of nine alkylsilanes in air at atmospheric pressure have been reported (84).

The CO-O_2 system still presents many unsolved problems. One difficulty is that great care is necessary to obtain consistent and reproducible results. For instance, Burgoyne & Hirsch (11) found that the reaction between dry CO and O_2 was very slow below 1050°C. but ~0.025 per cent added water caused ignition at 777°C. Methyl alcohol and formaldehyde strongly inhibited the reaction. Warren (85), using a vessel coated with boric acid, followed the explosion peninsular to lower temperatures than usual. Traces of water were essential for ignition under these conditions, and the results indicated that CO has a very high efficiency as a third body. The effect of additions on the glow and explosion limits has been investigated by Hoare & Walsh (86). A coating of PbO raised the lower glow limit markedly and slightly raised the upper limit. In the presence of water vapour they suggested that an excited CO_2-O_2 complex formed transferred energy to an H_2O molecule decomposing it into H and OH. Von Elbe *et al.* (87) and Gordon & Knipe (88) have made a careful study of the second explosion limit and have discussed termination reactions by which the limit is probably controlled.

The glow and explosion limits of CS_2-O_2 mixtures have been investigated by Webster & Walsh (89). The results were affected by the formation of solid on the walls, but consistent measurements were obtained by washing the vessel with 40 per cent HF between each run. The influence of inert gas on the ignition limits of dry cyanogen in air has been shown to be entirely due to a dilution effect (90) indicating that the explosion is predominately thermal in character.

The influence of various factors on the inflammation limits of CH_2O-O_2 mixture have been determined by Vanpee (91). The apparent temperature coefficients for the inflammation of CH_4, C_2H_6, C_5H_{12} and C_6H_{14} with oyxgen

have been measured (92). Kijama, Osugi & Teranishi (93) have determined the effect of water and carbon tetrachloride on explosion limits of acetylene and air or oxygen at pressures greater than atmospheric. The effect of temperature, pressure and composition on the lag before inflammation of C_3H_8-O_2 mixtures has been investigated in a flow system (94, 95). The delays, which were shortened by increase of temperature, propane pressure and oxygen pressure (slightly), were ascribed to the influence of branching reactions and heterogeneous destruction of chain carriers. The effect of tube material, fuel concentration and flow rate on the first and second stage ignition temperatures and on oxygen consumption for *n*-pentane and acetaldehyde-air mixtures fed upwards through vertical tubes is reported by King *et al.* (96). These authors suggested that ignition above 500°C. depended on the flammability of the boundary layer and that between 200°C. and 400°C. the reaction leading to inflammation was initiated by peroxides formed after aldehyde had been carried from the boundary layer in towards the centre of the reaction zone. Coleman & Stark (97) have studied the effect of CH_2ClBr and CCl_4 on the inflammation limits of *n*-hexane in air. A rapid compression machine has been used to measure the relatively long induction periods before reaction of cyclopentane and 2,2,4-trimethylpentane-oxygen mixtures (98).

The effect of water on the limits of flammability of the methyl alcohol-air system has been investigated (99). The products of the explosion of methyl nitrate in the gas phase at 300°C. have been shown to be NO, CO, H_2, H_2O, and CO_2 (100). Explosion was hindered by increase in the surface/volume ratio and by a PbO coating. Added inert gas or a little methyl alcohol aided explosion, but lead tetraethyl, formaldehyde, or NO_2 had no effect. A chain mechanism involving CH_3O radicals was proposed.

Dolan & Dempster (101) from a study of the effect of particle size of inorganic substances on their efficiency as suppressors of the spark ignited methane-oxygen explosion, concluded that the alkali halides were the most effective and that there was a direct relation between efficiency and the surface area of the powder.

The spark ignition limits of propane, *n*-butane, and *n*-pentane in air and oxygen has been investigated by Laffitte & co-workers (102, 103, 104, 105). The effect of tube diameter was studied with butane and with pentane and it was found that addition of N_2, A, and CO_2, but not of He, gave rise to a second inflammation region. The regions of flammability of hydrogen, cyanogen, methane, propane, butene, and propylene with N_2O are reported by Pannetier & Sicard (106). The effect of nitrogen and oxygen on the limits for C_4H_{10}-N_2O mixtures was also investigated.

Information concerning elementary reactions.—Theoretical consideration of the important part probably played by HO_2 radicals in slow combustion has been made difficult by the lack of precise knowledge of the dissociation energy of the H-O_2 bond. Indirect extimates have varied from 35–65 kcal. per mole. It is therefore of great importance that a reliable value of D(H-O_2)

$=49\pm2$ kcal. has been derived from measurements of ionisation potential of HO_2 and the appearance potential of the HO_2^+ ion (107). Robertson (108) has detected HO_2 radicals in the reaction of hydrogen and oxygen in a discharge tube and has calculated that about 1 in 10^5 collisions between H and O_2 give HO_2, the lifetime of the excited radical being $\sim5\times10^{-12}$ sec. The primary step in the reaction of oxygen atoms (produced by mercury-photosensitised decomposition of N_2O) with ethylene has been shown to be direct addition to the double bond (109). Oxygen atoms produced by the photolysis of NO_2 have been shown to be unreactive with ethane below 100°C. (110). Above that temperature some ethyl radicals were formed by the reaction $O+C_2H_6=OH+C_2H_5$, and this reaction was assigned an activation energy of <10 kcal. mole.

The reaction of oxygen with methyl radicals formed by the photolysis of acetone has been investigated at 120°C. and 175°C. by Christie (111). One molecule of formaldehyde and one of either CO or CO_2 resulted from the reactions of each CH_3 formed, and by labelling the end carbon atoms with C^{14} it was shown that the CO_2 was formed from the methyl groups probably via CH_3COCH_2 radicals. Hoey & Kutschke (112) used azomethane as the source of radicals and found that methyl alcohol was formed in high yield as well as formaldehyde. They calculated that the reaction $CH_3+O_2=CH_3O_2$ had zero activation energy and a steric factor 10^{-2}. They suggested that at room temperature the reactions

$$2CH_3O_2 = 2CH_3O + O_2 \text{ and } 2CH_3O = CH_3OH + CH_2O$$

occurred, but that at higher temperatures CH_3O_2 decomposed to give a radical which abstracted a hydrogen atom from azomethane. Christie (111) considered that CH_3O_2 either gave formaldehyde and an OH radical or reacted with acetone to give CH_3OOH, which decomposed into formaldehyde and water. Their conclusions are therefore not inconsistent.

A chromatographic study of the carbonyl compounds present in flames of various hydrocarbons and air, quenched by excess fuel, has indicated that HCO and RCO radicals are more stable between 500°C. and 800°C. than had been thought (113).

Alkoxy radicals are likely intermediates in combustion processes and it has been suggested that they can decompose giving an aldehyde, i.e. $RO=R'+R''CHO$ where R' and R'' are H atoms or alkyl radicals. Information about this reaction has been obtained from studies of the decomposition of alkyl nitrites or nitrates. The chemistry of nitrate esters has been reviewed by Boschan, Merrow, & Van Dolah (114). Gray has investigated the decomposition of alkyl nitrites (115) and Adler, Pratt & Gray (116) have identified the carbonyl products formed. It has been shown that the fission of an RO radical takes place at the carbon atom with the oxygen attached and the largest alkyl group splits off most readily. Gray has also discussed the thermochemistry of alkoxy radicals (117). The endothermicity and therefore probably the activation energies of the decomposition reactions decreased

as the number of carbon atoms increased. This agrees with the results of Levy & Adrian (118) on the decomposition of *n*-propyl nitrate, which indicated that the reaction $C_3H_7O = C_2H_5 + CH_2O$ was more rapid than similar ones of the lower radicals.

Flames and their Propagation

Flame theories.—Burgoyne & Weinberg (119) have carefully reconsidered the concept of excess energy held in flame fronts and have calculated values of this quantity and investigated its variation with mixture composition. They conclude that the criticism of Spalding (120) does not justify a rejection of the hypothesis. The effect of the magnitude of the activation energy on reaction rate has been examined by Weinberg (121) and rapid combustions discussed. The validity of one-dimensional flame front models is discussed by Fristrom (122), and studies of flow patterns through the front of a lean propane-air flame suggested that theories should be modified to include an area effect.

Smith (123) has given an exact treatment of the problem of a spherical diffusion flame, and this leads to a nonlinear ordinary differential equation of the second order. An analytical solution is presented in a form applicable to the experimental data and is applied to the method of temperature pattern measurements and to the calculation of rate constants. A mathematical analysis of ignition and combustion in a laminar mixing zone has been carried out by Marble & Adamson (124).

Decomposition flames.—It has been found that traces of air or oxygen are needed to maintain a stationary flame of hydrazine hydrate (125). Gray & Kay (126) have discussed the stability of the decomposition flame of pure liquid hydrazine and have shown that the flame speed relative to (*a*) the unburnt liquid is proportional to $p^{1/3}$ and (*b*) to the unburnt gas $p^{-2/3}$. The self-combustion of acetylene has been studied by measurement of the preignition kinetics and products and of the speeds of spark ignited flames in a tube (127, 128). Whereas addition of N_2 and propane decreased the flame velocity slightly and HBr and Br_2 considerably, increasing additions of O_2 and acetone caused the velocity to rise to a maximum. The carbon formed in the flames contained benzene and appreciable amounts of liquid polymer. They suggested that the self-propagation involves a free radical chain mechanism and that carbon is formed by the stripping of successive hydrogens from condensed acetylene radicals by free hydrogen atoms. A technique has been developed for stabilising a decomposition flame of ethylene oxide (129). The flame temperature was found to be 1182°K., and the measured dependence of the burning velocity on initial pressure and temperature has been discussed theoretically.

The decomposition flame of methyl nitrite (130) consisted of an orange flat disc with a conical afterglow of the same colour. Formaldehyde and NO were liberated. The flame had a rather precarious existence and is probably the slowest known (2.5 to 3 cm. $sec.^{-1}$). The stationary decomposition flame

of methyl nitrate has been maintained on a burner, and at low pressures the zones of reaction are clearly separated and have been studied spectroscopically (131). Strong formaldehyde bands are emitted from early stages of the flame. Wolfhard (132) has found that the burning velocity (7 cm. per sec.) of the ethyl nitrate flame was independent of pressure. Whereas the very low pressure flame had a single reaction zone, nearly invisible, and combustion was complete, at higher pressures there is a slow luminous reaction behind the flame front. Flame speeds in mixtures of methyl and ethyl nitrate vapours ignited by a spark have been determined by Adams & Scrivener (133), and the effect of inert diluents studied. The results were discussed from the point of view of the derivation of rate controlling steps from the measured velocities. Needham & Powling (134) have studied the decomposition flame of $EtONO_2$ stabilised at atmospheric pressure to give a flat stationary flame above the liquid surface. The large number of products of the combustion have been characterised and analysed. The experimental temperature distribution was in agreement with that calculated from the products. Ethyl nitrate was shown to be destroyed mainly by reaction with HONO and NO_2.

$$EtNO_3 + NO_2 \rightarrow HONO + C_2H_4ONO_2 \searrow$$
$$CH_3CHO + NO_2$$
$$HONO + EtNO_3 \rightarrow NO + H_2O + C_2H_4ONO_2 \nearrow$$

Results of the spectral study of the stationary flames of methyl nitrate (131) have been interpreted in terms of two general principles: (*a*) reluctance of NO to react except at high temperature; (*b*) the frequent occurrence of extensive pyrolytic reaction before the main reaction zone is reached.

Diffusion and premixed flames.—The heights of diffusion flames involving laminar flow and the relative importance of mixing and reaction rates have been considered theoretically by Powell (135). Using a probe combined with mass spectrometric analysis Smith & Gordon (136) detected CO, CO_2, water, unsaturated hydrocarbons, and small amounts of aldehyde in a paraffin candle flame burnt in air, and concluded that precombustion reactions involved cracking. It has been observed that the yields of hydrogen peroxide, aldehydes and acids from a hydrocarbon-oxygen diffusion flame are increased by an electric field (137). When a preheated H_2-air flame flowing at sonic velocity passed through an aerodynamic diffuser, it was observed that the speed was reduced and a stationary flame several decimeters long was formed (138). This flame was explored by means of a thermocouple and gas-sampling probe.

Prescott *et al.* (139) have determined composition profiles through the laminar front of a premixed C_3H_8-O_2 flame by means of a fine probe. As the probe was moved towards the centre of the luminous zone the concentrations of propane and oxygen decreased and those of H_2, CO, ethylene, and acetylene rose to a maximum. Probe sampling has also been used by Friedman & Cyphers (140) with lean low pressure C_3H_8-O_2 flames, and the results suggested that the hydrocarbon oxidised rapidly to CO with luminosity.

Flame velocities.—The form of the flame front propagated in tubes or between parallel walls has been discussed by Schultz-Grunow (141). He concluded that with parallel streaming a warped flame front might result and that it was inadmissible to rely on the normal velocity of propagation. Photographic and other techniques used in the study of the incipient phase of flame propagation have been considered by Gayhart *et al.* (142). Guenoche & Jouy (143) have discussed the accuracy of the tube method for the determination of flame speeds, and conclude that the most serious error which arises is in the determination of the flame front area. It has been found by Everett & Minkoff (144) that, when a methane-O_2 mixture in a tube was ignited by a spark, the flame travelled at normal speed and then accelerated. It was suggested that this was attributable to a change from a spherical to a cylindrical flame front. It has been shown that the velocity of combustion waves in acetylene-oxygen and propane-oxygen mixtures in tubes increased with increase in diameter (145). An experimental technique for the study of flame speeds by ignition of a small zone in a free jet of fuel and air by a single spark discharge has been described by Bolz & Burlage (146) and it was shown that experimental results were consistent, reproducible, and in agreement with those of other investigators.

The problem of spark ignition of combustible gases has been considered theoretically by Edmonson *et al.* (147). Manson (148) ignited a H_2-O_2 mixture at the centre of transparent latex balloons, and determined the forms and velocities of the combustion waves. The latter were found to be about the same as in tubes. The theory, apparatus, and technique of measurement of combustion velocity by the soap bubble method has been discussed and new developments of the method reported (149).

Weinberg (150) has discussed the location of the *schlieren* image of a flame, and Garner *et al.* (151) have deduced the burning velocities of ethylene, propane, and benzene-air mixtures from observation of the *schlieren* cones using the angle, and the frustrum and total area methods. Only the latter was found to give a value independent of the rate of flow of the unburnt gas, but the calculated velocities were too low when corrected for temperature. An adjustable flat flame burner for precise measurements of the burning velocities of slow flames has been described (152), and Botha & Spalding (153) have stabilised a flat propane-air flame downstream from a water cooled porous plate through which the mixture flowed. With this ingenious method it was possible to use a wide range of mixture ratios, and adiabatic flame speeds, obtained by extrapolation from the rate of heat extraction by the plate, were in good agreement with other work.

Many investigators have measured flame speeds in order to test the thermal conduction and the radical diffusion theories of flame propagation. The subject has been critically discussed and reviewed by Simon (154). The latest work tends to show that neither is exclusively correct but that thermal and diffusion effects may vary in importance according to the system. Van Tiggelen (155) and Luft (156) have discussed the use of burning velocities and of flame temperatures for the evaluation of activation energies of reactions

in flames. Van Wonterghem & Van Tiggelen (157) have studied C_2H_2-O_2-N_2, C_2H_4-O_2, and CO-H_2-O_2-N_2 flames to investigate the validity of the expression derived by Van Tiggelen (155) for the calculation of activation energies. They have derived values of the chain branching activation energies for a number of flame reactions from a study of the effect of diluents on the burning velocity. Anderson & co-workers (158, 159, 160) have determined the ratio of burning velocities of hydrogen-bromine and deuterium-bromine flames in a horizontal tube. They have calculated the velocities of these flames and that of H_2-Cl_2 mixtures from independent kinetic data. The radical diffusion theory gave values in fair agreement with experiment. Later work on the effect of nitrogen, argon, and helium on the H_2-Br_2 burning velocity, determined by the burner method, gave results which did not follow the patterns to be expected on the basis of either thermal or diffusion effects alone.

Wagner & Dugger (161) and Wagner (162) have measured the burning velocities of over forty organic compounds (including 33 hydrocarbons), either by the burner or horizontal open tube methods. The equilibrium flame temperatures and the active particle concentrations for mixtures, at which the maximum velocities occurred, have been calculated for 39 compounds. The measured velocities for hydrocarbons correlate better with the relative active particle concentrations than those for compounds containing oxygen and nitrogen. The Tanford-Pease equation was used in a modified form to calculate the burning velocities. Kurz (163) has investigated the influence of hydrogen sulphide and hydrogen selenide on the flame speeds of C_3 and C_4 hydrocarbons in air. Both compounds reduced the propagation velocity and it was suggested that this was a result of reactions such as

$$H + S_2 = HS_2 \qquad HS_2 + H = H_2 + S_2,$$

which reduced atom and radical concentrations.

Egerton & Lefebvre (164) have determined the burning velocities of methane, ethylene, propylene, and propane in air from the measured speed of uniform movement in a tube of rectangular cross-section. The effect of pressure and mixture strength was investigated, and the results indicated that both heat effects and diffusion, especially of hydrogen atoms, played a part in the flame propagation. However Badami & Egerton (165) from measurements of the velocities of the same hydrocarbons and those of carbon monoxide and cyanogen in air in a lower range, 4 to 8 cm. sec.$^{-1}$, by a flat flame burner method observed an approximate linear relationship between velocity and the heat generated or the maximum flame temperature. They suggested that for hydrocarbons the thermal theory was quite adequate to explain the velocities which were controlled by a reaction, preceding the sudden development of chain branching. With carbon monoxide, however, diffusion probably played a greater part.

Grosse & Kirshenbaum (166) have observed that with a H_2-F_2 premixed flame the burning velocity (estimated 10,000 cm. sec.$^{-1}$ at 25°C. for a 1:1 mixture) was far in excess of that of any other known flame, being about 10

times that of a H_2-O_2 flame burning under the same conditions. Burning velocities of hydrogen sulphide and ammonia in air or oxygen have been measured by use of a nozzle burner (167). Luft & Cohen (168) observed that the velocities of flat flames of ammonia in air were higher with excess air than with excess ammonia. Dugger *et al.* (169) found that the flame velocity of a preheated propane-air mixture increased with increasing initial temperature of the mixture and decreased with increasing time of heating, on account of preflame reactions. The fundamental flame velocity and its variation with composition has been measured for methylalcohol-air mixtures by Wiser & Hill (170), using the horizontal tube method.

Flame stability.—This subject has become increasingly important, especially from the point of view of combustion in jets, and falls naturally into three parts: quenching of flames by the wall, stability on burners, and the phenomenon of turbulence.

Berlad & co-workers (171) have derived equations for the quenching of gaseous flames on the walls of the containing vessel, using the active particle diffusion theory of flame propagation. Quenching was ascribed to efficient heterogeneous combination of hydrogen atoms or OH radicals. A relation derived from very simple heat theory by Peshkin (172) for the change in the lower limit of flame propagation with variation of the initial temperature of the burning mixture agreed with experiment for flames of carbon monoxide, methane, ethylene, and pentane. The minimum tube diameters for the propagation of ethylene-air flames, and also the critical flow rates for flash-back down cylindrical burner tubes, have been determined by Hoare & Linnett (173), who concluded that a portion of the mixture near the wall was not consumed by the flame. It has been shown that quenching by the wall was a major factor in controlling the pressure limits for the propagation of flames through propane-air mixtures in tubes of different diameters (174).

Anomalous stability data obtained with carbon monoxide-hydrocarbon-air flames can be explained if the reactants are converted to carbon monoxide-water-oxygen-nitrogen before the flame reaction (175). Kurz (176) has investigated the lean and rich blow-off and flash-back limits of shielded laminar flames of hydrocarbons and hydrogen sulphide in air and has found that the rich blow-off limits of ethylene-air flames (but not those of other hydrocarbons) are markedly extended by narrow shield tubes (177). The unique behaviour of ethylene in giving stable flames at compositions where the burning of other hydrocarbons is unstable is determined by the sensitivity of the cracking reaction to external influences. Blow-off limits using an inverted burner were found to be the same as those with an upright one (178). Kurz (179) has also studied the influence of the temperature of the unburned mixture on the blow-off limits for methane and propane flames using a vortex burner of special design. The limits of blow-off from a bunsen burner have also been reported by Thorpe & Browning (180), Grumer *et al.* (181), and Dugger (182). The latter investigated the effect of wall quenching and dilution by secondary air on a preheated propane-air flame.

Schaffer & Cambel (183) have found that an opposing jet is better than

a physical flame holder in stabilising combustion processes and have given blow-off data for different configurations and conditions. Lee *et al.* (184) have demonstrated several distinct modes of stability of propane-air flames in a ducted burner. In general the stability was controlled by the flow pattern at the inlet or by the duct-wall temperature if this was above about 900°C.

The general theory of flame stability has been examined by Rosen (185) and by Layzer (186). The latter has predicted that the sensitivity of a steady state deflagration wave to external influences depends on the shape of the temperature profile, but not on the speed or width of the wave or the pressure. Rosen has given a general numerical method for the determination of the stability of the steady-state flame and has obtained a simplified condition which permits the investigation of the stability as a function of fundamental physical parameters.

Barton (187) has derived equations for the shape of a turbulent diffusion flame, and Wohl (188) has attempted to obtain a reliable equation for the turbulent burning velocity of a passive flame front. He has derived a generalised form of the equation of Karlovitz *et al.* (189), and modified forms of the equations of Scurlock & Grover (190). Wohl & Shore (191) have tested their equations by measurements of the burning velocities of turbulent methane and butane-air flames.

A technique has been described for using helium, detected by a conductivity method, for measurement of the transverse turbulence intensity in flames (192). Results obtained with highly turbulent flames stabilised on various baffles in a duct showed that the amount of flame-generated turbulence detectable at a fixed point in the duct by this method was small. Olsen & Gayhart (193) have taken *schlieren* photographs of spark-ignited flame kernels propagating in a free jet of combustible gas, with laminar and turbulent flow, and have shown that turbulence distorted the flame fronts but caused no apparent change in the propagation rate. Mickelsen & Ernstein (194) have also measured photographically the growth rate of flames in a flowing turbulent stream of combustible gas and have studied the effect of fuel-air ratio and of the size of the turbulence generating grids. Their results indicated however that turbulence caused a reduction in the propagation rate owing to a diffusive effect which lowered the flame temperature.

Egerton & Lefebvre (195) have investigated conditions leading to vibrations and turbulence in the flame front of a hydrocarbon-air mixture burning in a tube. Botha & Spalding (196) observed that the front of a flat propane-air flame was cellular in form with some rich, stoichiometric and weak fuel-air ratios. The cell size varied with mixture ratio and rate of heat extraction by the cooled porous plate.

Spectroscopy of Flames

The emission spectrum of a flame is attributable to the activated particles present in the flame. In addition to the emission from simple molecules,

diatomic radicals such as OH, CH, C_2, CN, NH, CS, etc. are frequently observed and, in some cases, more complex emitters like CO_2, HCO, N_2O, NH_2, and CH_2O. In recent years the trend has been towards the quantitative determination of the concentration of emitters (and absorbers), i.e., the identification and relative population of the species in the different energy levels. For monatomic and diatomic emitters the identification can be carried out unambiguously, but this is not generally true with polyatomic molecules or radicals because of the complexity of the visible and ultraviolet spectra. In the latter respect measurement of the infra-red rotation-vibration spectra have been particularly useful. Although it is not necessarily true to say that the chemical species observed by special methods always play a vital role in the rate-controlling processes of combustion, detailed spectroscopic studies of flames do give much insight as to the nature of the reactions occurring and other valuable information such as flame temperatures and temperature profiles. Hydrocarbon flames have been extensively investigated in recent years. Marr & Nichols (197) have shown that the emission of light of λ 4050 Å by the O_2-C_2H_2 flame has an associated violet continuum which they ascribed to the emission of C_3. Kiess & Bass (198) believe this λ 4050 Å group of cometary spectra to be a Σ-Π transition of the linear C_3 molecule. Premixed C_2H_4-air flames with natural turbulence have been found to show the same qualitative spectra as laminar flames (199) and the 30 per cent reduction of the C_2, CH, and OH intensities is ascribed to quenching in the flame front. Madden & Benedict (200) suggest that the pure rotational lines of OH, observed in the emission from the C_2H_2-O_2 flame, might be used to determine the dipole moment of the OH radical. The self-absorption and linearity of the band spectrum of OH in flames has been investigated by Huldt & Knall (201). Gaydon & Guedeney (202) have shown that preheating a CO diffusion flame increased the intensity of the continuum, and this was interpretated as being caused by CO and O atom collisions at a repulsive energy surface. The absolute strength of the CO_2 band was unaffected by temperature, showing that the emission was not thermal in origin. The O_2 Schumann-Runge bands were strengthened as a result of thermal excitation.

Plyler (203) has summarised recent measurements of the infrared emission of hydrocarbon flames in the region 1 to 5.5μ. Flame temperatures, derived from the intensities of vibration-rotation bands, agreed with temperature measurements on incandescent particles in the C_2H_2-O_2 flame. A spectrophotometric study has been made by Wohl & Welty (204) of the structure of the burning and post-combustion zones of the butane-air flame with a flat flame front at 1 atm. pressure. Measurements in the infrared have been used to determine the temperature profile and in the visible and ultraviolet to follow the rise and decay of the flame radicals CH, C_2, OH, and of CO_2. Spectra of the C_2H_2-O_2 flame in the region 1.5 to 1.7μ by Benedict & Plyler (205) have shown that the most prominent feature of the emission was the vibration-rotation lines of OH, and the vibration-rotation temperature has been calculated to be 2600 ± 100°K. Using a flat diffusion flame of NH_3-

O_2, the emissions of OH, NH_3, H_2O and the absorptions of NH_3 and H_2O have been studied as a function of position in the flame (206). Combination of the results with the results obtained by Wolfhard & Parker (207) gave a complete description of the flame.

Infrared spectral studies appear to be a fruitful line of attack on the complex mechanism of low temperature oxidations. Using a flat flame burner as developed by Egerton & Thabet (208) for the stabilising of cool and two-stage flames of diethyl ether, Donovan & Agnew (209) have shown that carbonyl compounds are formed as intermediates and that the final products contain HCHO, CO_2, H_2O, CO, C_2H_4, CH_3OH and CH_4. The emission was shown to be of thermal origin, and the calculated temperatures were 700°K. for the cool flame and 1000°K. for the second flame. Burner and engine cool flames were compared. The ultraviolet absorption and emission as a function of time has been examined by Minkoff *et al.* (210) for the low pressure spark-initiated explosions of H_2-O_2, CO-O_2, and CH_4-O_2 mixtures. Measurement of the radiation (211) from the explosion of wet and dry CO-O_2 and CO-air mixtures with small amounts of added hydrogen has shown that the emission was chemiluminescent and occurred in the early stages of the reaction. The spectral emission and combustion mechanism in flames supported by oxides of nitrogen have been summarised by Wolfhard & Parker (212). It was shown that NO reacts in two ways: (*a*) by thermal decomposition, a process which does not occur below 2800°K.; (*b*) by reaction with radicals such as NH and NH_2 at much lower temperatures. Farber & Darnell (213) have recorded the emission spectra of NH_3-HNO_3, NH_3-NO_2, NH_3-O_2, N_2O, and NO diffusion flames. Hydroxyl bands were observed with NH_3-O_2 and NH_3-NO_2. Skirrow & Wolfhard (214) have studied the diffusion flames of H_2, CO, CS_2, CH_3OH, H_2O, NH_3, hydrocarbons, and organic halides with ClF_3. It was observed that carbon tetrafluoride introduced into the C_2H_2-O_2 flame led to the emission of CF and CF_2 bands and reduced carbon formation (215). With H_2-O_2 flames the principal emission was that of OH, and no radiation below 3000 Å was observed. The study of the structure and emission spectra of diffusion flames of $ZnMe_2$, $CdMe_2$, $PbMe_4$, $Fe(CO)_4$, and $Ni(CO)_4$ with O_2 and air alone and with additions of H_2, CH_4, CO_2, and acetaldehyde has shown that intermediate peroxides were the cause of the spontaneous inflammation of these substances at room temperature (216). Once the flame had been stabilised all the above substances decomposed spontaneously before oxygen reached this region of the flame.

Flame temperature.—The determination of flame temperatures has received much consideration and in this section spectroscopic and other methods are reviewed.

The existence of nonequilibrium conditions in fast reactions and thus the difficulty of defining "temperature" is now generally realised. The causes and results of departure from thermal equilibrium in a reaction zone of a flame has recently been fully reviewed by Shuler (217). In spite of these apparent difficulties the determination of the effective temperature in the

various forms the newly released energy takes is of importance in the understanding of the mechanism of flame propagation and flame properties. One of the convenient and commonly used methods for the measurement of flame temperature is that of the spectrum line reversal method which gives the effective electronic excitation temperature. Further measurements by this procedure have been reported. Bauserman *et al.* (218) claim to detect 25°K. temperature and 3 msec. time differences in rapidly varying flames. Strong & Bundy (219) have described an apparatus for the determination of the temperature in flames of complex structure, and Huldt & Knall (220) have measured the contour of the Na lines for air-C_2H_2 flames.

The spectra of CH in flames of C_2H_2, CH_4, and C_3H_8 with O_2 have shown that the R branch $^2\Delta$-$^2\Pi$ is unreliable as a temperature indicator (221). The effect of self absorption on the rotational temperature of CH in C_2H_2-O_2 flames has been calculated by Broida (222) for the hot gases above the reaction zone, and the calculated temperatures have been shown to be in agreement with experiment. In the reaction zone the rotational temperature was several hundred degrees higher than the adiabatic temperature.

Among the rotational anomalies in spectra is the high rotational temperature of OH in the reaction zone of hydrocarbon flames. The relevant experimental evidence has been critically reviewed by Penner (223). Elliott & Penner (224) have discussed the effect of adjacent radiating and absorbing regions on the apparent rotational temperature without reaching a definite conclusion. Experimental measurements by Penner & Bjornerud (225) with C_2H_2-O_2-A, and C_2H_2-O_2-H_2 flames at atmospheric pressure show that an unequivocal quantitative estimate of the rotational temperature and OH concentration cannot be made. The results gave an upper limit to both quantities and led to reasonable rotation temperatures at the tip of luminous flames. Flame temperatures calculated by Ketelaar *et al.* (226) from the OH rotational spectrum of O_2-H_2 flames agreed with ultraviolet measurements.

Moutet (227) has reviewed optical methods, and Pepperhoff & Grass (228) have stated that the colour pyrometer is the only instrument useful for the determination of the colour and black temperature of an inhomogeneous flame. They have developed a theory for the calculation of the true spectral radiation intensity and the total radiation intensity. Sviridov & Sobolev (229) have worked out a photographic procedure for the measurement by the inversion method, which does not require equalisation of temperature. A method of recording the variation of temperature through a plane flame by refractive index gradient measurement, combined with accurate observation of the initial temperature, has been reported (230). The method was applied to a very lean ethylene-air flame and the variation of reaction velocity with temperature and fraction of reaction was calculated from the temperature distribution, burning velocity and physical properties of the gases. An apparatus and technique has been described for the determination of the temperature profiles of flames by the particle track method (231).

Rounthwaite (232) and Miao *et al.* (233) have investigated the tempera-

tures of flames from spark-ignited explosions. The former made simultaneous resistance wire measurements with two quartz-covered platinum wires of different diameters and obtained reasonably accurate results for the CO-O_2 explosion. The latter used a modified Na-D line method to measure the temperatures at several radii in a spherical vessel. With a methane-oxygen mixture the observed temperatures were about 5 per cent lower than the calculated values near the centre and fell off rapidly as the walls were approached.

The temperature pattern of a very lean propane-air flame, measured by a thermocouple, has been analysed mathematically to obtain the pattern of the heat release rate (234). The maximum flame temperature observed was 1605°K., and the burning velocity varied as $1/p^{0.3}$. The flame temperature of 4640 ±150°K. at one atmosphere (calculated, 4835 ±50°K.) observed with a 1:1 C_2N_2-O_2 mixture is one of the highest obtained by chemical reaction (235). The temperature was increased to 5050°K. by preheating the gases to 100°C.

The effect of noncombustible materials on flames of H_2, CO, CH_4 and C_2H_4 in air has been investigated by Burdon *et al.* (236) and by Simmons & Wolfhard (237). Methyl bromide and bromine raised the temperatures near the flammability limit as a result of a specific chemical inhibiting action. Quenching occurred when this temperature exceeded the adiabatic flame temperature. Burdon *et al.*, concluded that the chain breaking step with methyl bromide added to a H_2-O_2 flame was $H+CH_3Br=HBr+CH_3$ but that in a CO-O_2 flame it merely competed with the CO for the available oxygen.

Flash photolysis.—The method of flash photolysis developed by Norrish & Porter (238) has been successfully used in the study of explosions by measurement of the time variation of the absorption or emission spectrum. All the common diatomic radicals (OH, CH, C_2, CN, NH, etc.) have been observed by this method and the variation of the intensity of absorption or emission with time and mixture composition has given valuable data. Results have been reported for the explosion of C_2H_2, C_2H_4, and C_2H_6 with oxygen initiated by flash photolysis of NO_2 (239). The time-concentration curves of the diatomic radicals (OH, CN, NH, CH) were similar in the four hydrocarbons, but there were important quantitative differences in the stiochiometry of the mixtures which gave equivalent spectroscopic results. The continuous spectra present after the explosion was shown to result from the absorption by C_3 and carbon particles. A second intense continuum at 3900 Å whose occurrence followed closely that of the radicals C_2 and C_3, was attributed to a carbon molecule which was in approximate thermal equilibrium. Porter (240) has discussed the problems of the identification of free radicals by spectral methods and has raised the question as to whether certain bands in flames of C_2H_4 are attributable to HCO or HCHO. Hanst & Myerson (241) have adapted the flash technique to the study of explosions induced by thermal energy of gases at the temperature of mixing and have

measured the concentration of radicals and other short-lived species as a function of time in CS_2-O_2 mixtures.

Microwave measurements.—Sugden (242) has summarised the measurements he and his collaborators have made on ionisation in flame gases using the technique of microwave absorption to measure the concentration of free electrons generated by the use of controlled amounts of alkali metals introduced into the premixed gases before combustion. The electron concentration was shown to be consistent with the establishment of thermodynamic equilibrium. A similar conclusion has been reached by Shuler & Weber (243) from a study of the ionisation in premixed H_2-O_2 and C_2H_2-O_2 flames. Kuhns (244) has described the use of the microwave absorption method for the measurement of temperatures of 2000°K. to 3000°K. and claims an accuracy of ±60°K., changes of temperature of ±5°K. being detectable. A photometric investigation of the state of alkali metals in hydrogen flame gases (245) has shown that above 2000°K. the equilibrium $MOH \leftrightharpoons M + OH$ was fully established. The electron affinity of OH was calculated to be 65 ±5 kcal.

Propellant Burning

The design and development of rocket motors of high combustion efficiency has led to increased study of the fundamental characteristics and mechanism of the burning of liquid and solid propellants. The simplest class of propellants are the nitrate esters, the thermal energy of combustion in this case being released by chemical reaction of the oxygen of the nitrate group and the carbon and hydrogen of the organic part of the molecule. The investigations of the decomposition flames of methyl nitrate, methyl nitrite, ethyl nitrate, and the measurements of flame speeds in esters have been discussed in a preceding section. Adams & Wiseman (246) have reviewed their work on the combustion of simple liquid nitric esters and have discussed the relationships between the rate of burning, chemical structure, and heat of explosion. Steinberger & Carder (247) have measured the temperature profiles of liquid nitrate esters burning as strands in glass tubes and at pressures of 15 to 1000 p.s.i. by the use of fine thermocouples. The temperature at the liquid interface was approximately the same as the ambient temperature, and it was suggested that reaction at the liquid surface was brought about by the back diffusion of free radicals from the flame zone. Hildenbrand *et al.* (248) have used a similar thermocouple method to explore the temperature distribution in burning liquid strands of 2-nitropropane with either HNO_3, nitroethane, or metriol-trinitrate. The results were explained in terms of a thermal model.

Temperature measurements and gas sampling tubes have been used to study the combustion of ammonia-liquid oxygen mixtures in a rocket chamber (249). McCullough & Jenkins (250) have discussed the techniques which are useful for the study of the combustion of hypergolic (self-ignition on mixing) liquid combinations. A development of the mixing technique of Roughton, Chance, and others has been used by Kilpatrick & Baker (251) to

investigate the self-ignition of anhydrous hydrazine with 100 per cent nitric acid. Several methods have been described for the measurement of ignition lags for liquid propellants. Hicks (252) has considered the thermal theory of solid propellant ignition and has examined the influence of the temperature of the propellant on the ignition time. The temperature and composition of the gas phase region of a burning nitrocellulose-nitroglycerine propellant, measured by a thermocouple and probe, has shown the presence of three well-defined reaction zones (253). Steinberger (254) has discussed the mechanism of burning of double base propellants and has concluded that propagation with liquid nitrate esters occurs by a diffusion process. The initial reaction postulated was the attack of atomic hydrogen on the ester. An excellent and thorough discussion of the mechanism of the combustion of solid propellants has been given in two review papers by Geckler (255).

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HIGH TEMPERATURE CHEMISTRY[1]

By Leo Brewer and Alan W. Searcy

Department of Chemistry and Chemical Engineering and Division of Mineral Technology, University of California, Berkeley, California

The term "high temperature chemistry" is best defined not in terms of a temperature range, but in terms of characteristic chemical reactions. At room temperature, one is accustomed to each element having characteristic oxidation states and compounds. As the temperature is increased, most chemical systems undergo changes and at high enough temperatures the characteristic oxidation states and compounds are usually different from those found at room temperature. The term "high temperature chemistry" as used in this paper will refer to the chemistry of systems at sufficiently high temperatures so that the oxidation states, compounds, and general chemical behavior differ appreciably from those at room temperature. In some systems like the Al—Cl system, a temperature only slightly above room temperature yields stable compounds of aluminum in the 1+ oxidation state which are unstable at room temperature. In other systems, the temperature must be raised several thousand degrees before the important stable species differ appreciably from those important at room temperature.

High temperature chemistry is in a rather primitive state at present. In many important systems, the major stable species are not yet known. Reliable thermodynamic calculations cannot then be performed since the correct net reactions are not known. A great deal of effort in the high temperature field is devoted to the elementary task of simply fixing the formulas of the important species.

Due to limitations of space, our review must be limited to several groups of related papers. Thus many interesting isolated papers as well as important topics such as kinetic effects at high temperatures have been omitted. Fortunately most of these topics are being covered in other chapters of this volume. In this review attention will be largely concentrated on the problems of identifying the compositions of high temperature phases and gaseous species and of determining their thermodynamic stabilities. It is convenient to consider gaseous and condensed phases separately.

High Temperature Gaseous Species

In the past, the use of optical spectra has been one of the most powerful tools for the study of high temperature gaseous species. However this method has limitations and one of the most important developments in high temperature chemistry has been the use of the mass spectrometer for identification of the gaseous species present in high temperature vapor (1 to 5). The combination of optical and mass spectrometric methods should greatly accelerate the elucidation of high temperature gaseous systems.

[1] The survey of the literature was concluded in January, 1956.

The mass spectrometer method consists of the ionization of the high temperature vapor by electrons and identification of the resultant ions. Because of the many complications due to fragmentation of molecules by electron impact, due to possible chemical reactions within the ionization chamber of the mass spectrometer with the hot filament, and due to background impurities, conventional mass spectrometers are not easily applicable to quantitative treatment of high temperature problems. Inghram and his group (1, 2, 3) have designed a mass spectrometer that appears to meet most objections. One of the main features is the use of a well-collimated molecular beam that traverses the ionization chamber without hitting the entrance and exit slits of the ionization chamber. The high temperature beam is exposed to electron bombardment only during the time of transit through the ionization chamber. There is thus no opportunity for the material to react with the walls of the ionization chamber or with the filament supplying the electrons.

Another important feature is the increase of the sensitivity of the apparatus to allow use of electrons of only a few volts energy rather than the customary 50–100 volt electrons. Use of low voltage electrons eliminates many fragmentation processes. To minimize background contamination, a shutter is used to modulate the molecular beam to distinguish between products from the molecular beam and those from the general background. One difficulty is that the high concentration of photons in high temperature beams sometimes produces photo-ionization of molecules before the point of intersection with the electron beam, causing deflection to a position of incorrect mass. Because of the high sensitivity of the mass spectrometer, it is possible to study systems at much lower pressures and therefore lower temperatures than is possible by other methods. Thus container problems are minimized but volatile impurities are more troublesome. However, knowledge of isotopic abundances often allows one to distinguish between different species whose most abundant masses coincide. Separated isotopes can also be of value in confirming identifications.

Normally the mass spectrometer suffers from its inability to provide absolute concentrations or partial pressures of the species being studied. To obtain the heat of formation of a gaseous species, one cannot easily use the Third Law of Thermodynamics and must resort to determination of temperature coefficients of ion currents to obtain heats through the Second Law of Thermodynamics. Because of the difficulty of obtaining accurate temperature measurements, such heats can be considerably in error. Inghram and his group (3, 5) have attempted to use the Third Law by calibrating their apparatus with a substance of known vapor pressure such as silver and comparing the ion currents due to silver ions with the currents due to the species under study at a series of bombarding electron voltages. For an absolute calibration, one must know the ratio of cross sections of silver to that of the species under study with respect to ionization by electrons. By assuming that the maximum cross sections obtained at the most efficient electron

voltages are simply related to the geometrical cross sections, it is possible to obtain absolute concentrations. With these, together with entropies that are readily available, one can calculate heats. This method is obviously not a rigorous one, but it can be very useful as a check of the reliability of heats obtained by use of the Second Law of Thermodynamics. To illustrate the range of uncertainty that can be allowed in fixing the ratio of ionization cross sections, an error of a factor of two in the cross section ratio and thus in the absolute partial pressure results in an error of only 1.3 kcal. at 1000°K. and 2.6 kcal. at 2000°K. Since the heats obtained from the Second Law measurements are often uncertain by more than 10–20 kcal., the use of the Third Law is quite desirable.

One of the most fruitful applications of the mass spectrometer has been the elucidation of the gaseous species of oxide systems. Brewer (6) has reviewed the oxide data available up to 1952. As most of the developments since then have been reported during the last year, the following review of various gaseous oxide studies will be restricted largely to 1955. The oxides will be reviewed in the order of their position in the periodic table, considering mass spectroscopic studies together with other types of study.

Brewer & Margrave (7) determined the vapor pressures of Li_2O and Na_2O. Van Arkel, Spitzbergen, & Heyding (8) have confirmed the order of magnitude of the vapor pressure of Li_2O. Both groups have evidence for volatile hydroxides in agreement with the flame work of Smith & Sugden (9). The present data are not inconsistent with vaporization to the gaseous elements, which would indicate that Li and Na metal atoms do not react with oxygen to form any important volatile oxides. Brewer & Margrave (7) present theoretical calculations that indicate that K_2O, Rb_2O, and Cs_2O likewise do not exist as stable gaseous molecules although there is a possibility that KO, RbO, CsO and even LiO gases might be stable. All of the alkali hydroxides appear to exist as stable gaseous molecules (7, 10). An interesting development has been the demonstration by James & Sudgen (11), Gaydon (12), and by Lagerqvist & Huldt (13), that flame spectra formerly believed due to alkaline earth oxides are indeed due to alkaline earth hydroxides of the formula MOH. The thermodynamic stabilities are not yet known. A mass spectrometer examination of alkali oxide and alkali and alkaline earth hydroxide vapors would be of great importance for confirmation of these conclusions.

Porter, Chupka & Inghram (14, 15) have subjected the vapors of MgO, SrO, and BaO to electron bombardment and have examined the resulting ions in the mass spectrometer. The barium oxide results are most spectacular in that the gaseous species Ba_2O, Ba_2O_2, BaO, and Ba_2O_3 have been observed. Ba_2O predominates under reducing conditions, BaO predominates under neutral conditions, and Ba_2O_3 is the dominant species under oxidizing conditions. Comparison of the Ba_2O heat with that calculated (16) on the basis of a linear ionic model indicates that the unpaired electrons of Ba^+ must be participating in bonding, possibly in a manner similar to mercurous ion. The

most reasonable electronic model for Ba_2O_2 would involve peroxide oxygen rather than Ba^{+3}

The other alkaline earths have not been studied as thoroughly. Only the diatomic molecules have been observed so far. According to the mass spectrometer results, barium oxide is the only alkaline earth oxide vaporizing predominantly to a gaseous oxide molecule while MgO, CaO, and SrO vaporize predominantly to the elemental species under neutral conditions.

It is difficult to use the available optical spectroscopic data to check the mass spectrometer results. Only the singlet systems of the alkaline earths are observed, but it now seems clear that the ground states are mostly triplets. Brewer & Porter (17) and Lagerqvist & Huldt (18, 19) find the lowest $^1\Sigma$ states of MgO, CaO, and SrO to be several volts above the ground states. It is clear that the dissociation limit of the lowest singlet states of MgO, CaO, and SrO must correspond to one of the many highly excited atomic products. A D_0 value can therefore not be derived. There are enough data for BeO so that Lagerqvist (20) believes that a dissociation energy of 4.8 *ev* can be established for the $^1\Sigma$ state, but its excitation is unknown. The $^1\Sigma$ state of BaO is the ground state and the spectroscopic data can be used to obtain a dissociation heat that is in agreement with mass spectrometer, vapor pressure, and flame measurements.

Although it would not be difficult to reconcile the available vapor pressure, flame, and spectroscopic data on the basis of BeO, MgO, and CaO vapors consisting predominantly of the elemental species under reducing or neutral conditions, there appears to be an unresolved discrepancy for SrO. Huldt & Lagerqvist (21, 22) and James (23) have determined the concentration of uncombined strontium atoms in flames and are in agreement on a D(SrO) of around 5 *ev*. From this value, one can calculate that strontium oxide should vaporize predominantly to SrO molecules, but the flame work of this type tends to yield D_0 values that are somewhat high. The only clear-cut experiments which can be compared with the mass spectrometer work are the vapor pressure measurements using the Langmuir method by Claassen & Veenemans (24) and Moore, Allison & Struthers (25). If one accepts the conclusions of Porter, Chupka, & Inghram (14) that the vapor pressure of SrO is due predominantly to dissociation to Sr atoms and a mixture of O atoms and O_2 molecules, one can recalculate the various experimental results to obtain the partial pressure of atomic Sr in equilibrium with SrO at 2100°K.: Claassen & Veenemans (24) find 3.8×10^{-5} atm., and Moore, Allison, & Struthers (25) find 2.3×10^{-5} atm. The results of Porter, Chupka, & Inghram (14) yield 1.0×10^{-5} atm. From the heat of formation of SrO solid and the heat of sublimation of Sr, one calculates 0.45×10^{-5} atm. Sr. Thus the observed total vapor pressures are larger by a factor of 5 to 8 than the vapor pressure expected if no important strontium oxide molecules exist.

In order to attribute the difference to error in the thermodynamic data, one would have to lower either the heat of sublimation of Sr or the heat of formation of SrO by over 9 kcal. The heat of formation of SrO has been well

checked. The determination of the vapor pressure of Sr by Hartmann & Schneider (26) has been confirmed recently by Priselkov & Nesmeyanov (27). It is very unlikely that these determinations are sufficiently in error to account for the SrO discrepancy.

There is likely some error in the temperature scale used by Moore, Allison & Struthers (25), but an error of 200° would be required for reconciliation of their results with the assumption of complete dissociation to the elements. Oxide vapor pressures tend to be high due to the prevalence of reducing conditions. Thus the vapor pressures of MgO reported by Brewer & Porter (17) are too high, undoubtedly due to reduction as well as an error in their temperature scale due to changes in radiation constants. The vapor pressures of SrO given by Claassen & Veenemans may be high for the same reasons. However, Moore, Allison, & Struthers (25) showed that they were not getting any reduction.

Morgulis, Gavrilyuk, & Kulik (28) have found that SrO has a small vaporization coefficient and claim that SrO vapor is largely undissociated. The complication of a low vaporization coefficient for SrO plus reducing conditions in the cell might cause an error in the mass spectrometer results. However, until further work has been done, it would seem that greater weight should be given to the mass spectrometer results.

It is still not possible to give very accurate heats of dissociation for the diatomic gaseous alkaline earths, but the following would seem to be the best available now: $D(\mathrm{BeO}) < 5$ *ev*, $D(\mathrm{MgO}) < 4$ *ev*, $D(\mathrm{CaO}) = 4 \pm 0.5$ *ev*, $D(\mathrm{SrO}) = 3.6 \pm 0.2$ *ev*, and $D(\mathrm{BaO}) = 5.65 \pm 0.2$ *ev*, where $^3\Sigma$ ground states are assumed except for BaO ($^1\Sigma$).

Soulen, Sthapitanonda, & Margrave (29) have measured the vapor pressure of boron oxide and have demonstrated that the principal species under oxidizing conditions is B_2O_3. Porter & Inghram (30) have confirmed this with the mass spectrometer. In addition they have obtained the most unexpected result that under reducing conditions B_2O_2 is much more important than the diatomic BO which has been known from its electronic spectrum for a long time.

The stability of Al_2O gas has been confirmed by the vaporization studies of Cochran (31) and by the mass spectrometer studies of Porter, Schissel & Inghram (32), but no other aluminum oxide species have been detected. White (33) finds AlO bands in burning aluminum but Cochran (31) does not observe AlO bands in furnaces at a lower temperature and AlO may not be present in appreciable concentrations. A mass spectrometer study under oxidizing conditions would be useful. On the basis of present information, all available data for Al—Al_2O_3 systems can be reconciled to the single gaseous oxide molecule Al_2O.

A mass spectrometer study of the lanthanum oxide system by Porter & Inghram (30) has found only the molecule LaO. It is of interest to note the change in the major species under reducing conditions in the third group of the periodic table from B_2O_2 to Al_2O to LaO.

A mass spectroscopic study of the Si—O system by Porter, Chupka, & Inghram (5) has confirmed that SiO is the predominant gaseous oxide species when either a mixture of Si and SiO_2 or SiO_2 alone is vaporized. In addition, minor constituents Si_2O_2 and SiO_2 were detected. The mass spectrometer work yields a heat of formation of SiO gas in excellent agreement with earlier determinations.

Phillips (36) has established the triplet state of TiO as the ground electronic state by determination of the temperature coefficients of triplet and singlet bands under equilibrium conditions. Osborn (37), Gilles & Wheatley (38), and Groves, Hoch & Johnston (39) are in agreement on the vapor pressures over various portions of the Ti—O system. The TiO molecule has been shown to be the predominant gaseous species over the TiO phase region. The TiO_2 gaseous molecule appears to predominate under oxidizing conditions.

Hoch, Nakata & Johnston (40) have measured vapor pressures in the Zr—ZrO_2 system in Ta metal containers. Their reported pressures are undoubtedly high because of reduction by the Ta.

Hoch & Johnston (41) have also determined the vapor pressure of ThO_2 obtaining a vapor pressure 40 times larger than that determined earlier by Shapiro (42). From the experimental details, it is clear that Hoch and Johnston are in error. Shapiro reports some reduction of ThO_2 by tungsten. Hoch and Johnston claim to disprove this by obtaining the same volatility for ThO_2 as for a ThO_2+W mixture. However, since Ta metal, which is considerably more electropositive than W, was used for the containers, Hoch and Johnston were merely measuring the vaporization due to reduction of ThO_2 by Ta in both experiments. No conclusions can be drawn from the available data about the formula of the vaporizing molecule although the magnitude of the vapor pressure reported by Shapiro indicated that ThO_2 does not vaporize by decomposition to the elements but must form a stable volatile oxide of some type.

There has been little new work on the gaseous oxides of the remaining transition metals. Premaswarup (43, 44) has analyzed several TaO bands and has obtained energy levels analogous to those for VO and NbO but no thermodynamic data are available. Considerable work has been done with the fourth group oxides and sulfides. Schumb & Bernard (45) have prepared gaseous SiS by reaction of silicon with silicon disulfide. Through reaction of H_2S with the appropriate metal or metalloid, Gastinger (46) has prepared not only gaseous SiS and GeS but also gaseous Al_2S and In_2S. The most systematic study of the oxides and sulfides of the fourth group elements has been by Barrow and his group at Oxford. Recent papers by Barrow & Rowlinson (34) and Barrow, Dodsworth, Drummond & Jeffries (47) have summarized the spectroscopic and thermodynamic properties of these compounds. In almost every instance, the diatomic molecules are the most important chemical species. Dressler (48) and Dressler & Miescher (49) have studied oxides and sulfides of phosphorus and they believe that

D(PO) is about 5.4 *ev.* Huffman *et al.* (50) have determined the heat of formation of PN gas from high temperature equilibrium measurements. An interesting study of the high temperature dissociation of SO_2 by St. Pierre & Chipman (51) has yielded a value of the heat of formation of SO through which the heat of dissociation of S_2 has been fixed. The recent demonstration of the high temperature importance of S_2O by Myers & Meschi (52) does not affect the calculations or conclusions of St. Pierre & Chipman as S_2O would be a minor contributor under their conditions. Soulen, Sthapitanonda, & Margrave (29) find TeO_2 gas to be stable even up to 1211°K.

Hornbeck (53) has extended the number of known vibrational levels of the ground state of OH and suggests that the accepted value of the dissociation energy of OH be increased. As OH is an important constituent of most flames, such a change would alter calculated compositions of flames considerably. However, the shorter extrapolation of the vibrational levels of the excited state of OH should be much more reliable than the long extrapolation required for the ground state data and it seems unlikely that D(OH) could be as high as suggested by Hornbeck.

More scattered, but very interesting, information on other types of high temperature gaseous molecules has been published in the last year or two. Again, mass spectroscopic and optical spectroscopic investigations have been among the most informative.

Schäfer & Hönes (54) have succeeded in preparing FeI_3 gas and Fe_2I_6 gas although ferric iodide has not yet been made as a condensed phase. Gregory & MacLaren (55) have studied the equilibrium established when bromine is passed over $FeBr_2$. The major gaseous species is Fe_2Br_6 under their conditions. They also determined the heat and entropy for the dissociation of Fe_2Br_6 (g) to $FeBr_3$ (g). Friedman (56) has obtained heats of sublimation to LiI and Li_2I_2 by means of a mass spectrometer. The partial pressure of Li_2I_2 is roughly equal to that of the monomer. A smaller concentration of Li_3I_3 is also detectable.

A mass spectroscopic investigation by Rosenstock *et al.* (57) confirmed the earlier work of Brewer and Lofgren who used the mass action law to show that the major species above cuprous chloride is a trimer. Rosenstock and coworkers also found trimers to be the main species in cuprous bromide and cuprous iodide vapor under conditions of rapid evaporation. Smaller concentrations of ions that probably were produced partly from ionization of monomeric and dimeric species and partly from fragmentation of trimers were observed. The chloride and bromide vapors appear even to contain appreciable concentrations of tetramers, and mixed halide gas species were produced by heating a filament coated with both cuprous chloride and cuprous bromide. Wong & Schomaker (58) have found by use of electron diffraction that $(CuCl)_3$ has a puckered ring structure.

Hobson (59) has observed a variety of both positive and negative ions resulting from bombardment of alkali chloride vapor by electrons in a mass spectrometer. He believes, however, that a considerable fraction of the com-

plex ions are produced by combination of ions and molecules in the mass spectrometer. Such combinations are negligible in experiments for which lower pressures are used. O'Konski & Higuchi (60) calculate theoretically an energy of dimerization for sodium chloride vapor that is high enough to indicate dimers should be observable in mass spectroscopic experiments. The generalization can probably be made that dimers can be expected to reach considerable concentrations in the saturated vapor of any molecules that have large dipole moments. Recent examples noted earlier are Ba_2O_2, B_2O_2, and Si_2O_2 in addition to the many halide dimers.

The NaF—AlF_3 and NaCl—$AlCl_3$ systems each yield tri-elemental gas molecules which seem to be $NaAlF_4$ [Howard (61)] and $NaAlCl_4$ [Dewing (62)]. Scattered reports of complex salt gas molecules have appeared from time to time for many years, but apparently the structures of none of them have ever been determined. The complex tetrahalides must almost certainly contain essentially tetrahedral AlX_4 groups, but the orientation of the tetrahedra with respect to the sodium is a very intriguing question. The bond to sodium is probably highly ionic, and it seems possible that the AlX_4 group may rotate with respect to the Na—AlX_4 axis. Motzfeldt (63) has examined Na_2CO_3 vapor and concludes that it consists of Na, O_2, and CO_2 gases. However, he finds that there is considerable resistance to the change from Na^+ and $CO_3^=$ ions in the melt to the gaseous species, and a mass spectrometer analysis of the vapor from a Langmuir type experiment would be of interest to determine if possible molecules like NaO or even ionic species might be intermediates in the vaporization process.

The equilibria among solid and gaseous species of the titanium-chlorine system have received considerable attention, Skinner & Ruehrwein (64), Farber & Darnell (65). Altman, Farber, & Mason (66) review and evaluate the literature on the problem. Untangling the stability relationships has been especially challenging because of the unusual difficulties encountered. In particular, both $TiCl_2$ and $TiCl_3$ vaporize to a mixture of gaseous products. Because of the complexity of the system and because of its industrial importance, more work can be expected. The heat and entropy of formation of gaseous $SiCl_2$ have been measured by Schäfer & Nickl (67) and Antipin & Sergeev (68). Equilibrium constants for the reaction $Si(s)+SiCl_4(g) = 2SiCl_2(g)$ are reported in the latter study which are considerably higher than those reported in the other study.

Zeeman (69) has observed and analyzed an emission spectrum attributed to AlC. His work is the first report of a specific gaseous metal carbide molecule. His value $D_0(AlC) = 1.6 \pm 0.2$ *ev* is far too low to account for the high concentration of carbon which has been reported in the sublimate from heating Al_4C_3 to 1800–2200°C. (70). If the observed transport of carbon does not proceed through CO disproportionation due to oxide impurity, one must conclude that either the observed transitions for AlC do not involve the ground state, or there are as yet unidentified species above Al_4C_3.

It is probable that more gaseous carbides and nitrides will be identified

within the next few years, but recent searches for gaseous metallic nitrides have yielded negative results. The nitrides Mg_3N_2 [Soulen, Sthapitanonda & Margrave (29)] and TiN and ZrN (71) are all reported to vaporize primarily by dissociation. The heat of formation calculated for ZrN by Hoch & co-workers (71) is about 6.7 kcal. lower than was recently obtained calorimetrically in K. K. Kelley's laboratory [Mah & Gellert (72)]. The discrepancy in heats is probably explained by the fact that Hoch and coworkers believed the solubility of nitrogen in zirconium to be low, and therefore did not correct for the reduction in activity of zirconium metal due to the solubility of nitrogen in the zirconium phase. The composition of the nitrogen-saturated metal is reported to be close to Zr_2N [Schönberg (73)].

The possibility that gaseous nitride molecules were present at concentrations lower than the concentrations of the elements cannot be precluded from the vaporization data. Stability ranges for a number of metal nitrides have been calculated by Margrave & Sthapitanonda (74) with use of estimated interionic distances and the assumption of singly charged ions. Revisions (75) of the original calculations of their note indicate that metal nitride molecules must be minor species in the 5000 to 40,000°K. range and can be important at lower temperatures only if the dissociation energies are higher than calculated from the singly charged ionic model.

Recent investigations have demonstrated that the vapors of many of the pure elements contain a variety of molecular species. For some elements that have in the past been assumed to vaporize only as atoms, molecule concentrations are high enough to affect significantly thermodynamic calculations. Of the carbon family elements, carbon, silicon, germanium, and tin have been investigated for vapor complexity. All showed a variety of vapor species.

A most interesting by-product of the mass spectrometer studies of the heat of sublimation of carbon to be discussed below has been the demonstration of the importance of C_3 and perhaps even of C_5 in addition to C and C_2. Furthermore, Honig (4) has found appreciable amounts of thermal ions in carbon vapor ranging from C^- to C_8^-. SiC_2, an analogue of C_3, has also been demonstrated through its spectrum by Kleman (76). If the observations of Inghram & Chupka (1, 2, 3) of a C_5 molecule with a very low vaporization coefficient can be verified and differentiated from possible TiC impurities, a ready explanation of the abnormally high vapor pressures obtained under essentially static conditions is available (77).

C_3 has been shown to have a discrete spectrum (78) that has been observed in comets and other astronomical bodies (79), and which has also been found in flames (79) and by Garton (80) in a high temperature furnace. In addition, Phillips & Brewer (81) have found a very strong continuous spectrum in carbon furnaces which they established as being due to C_3 by application of the mass action law. This spectrum has now been observed in other thermal sources such as flames (82) and has been shown by McKellar & Richardson (83) to be the cause of the high ultraviolet absorption observed

in carbon stars. It is not yet possible to give accurate figures for the contribution of the higher carbon species to the total vapor pressure, but the best available data would indicate the following partial pressures for saturated carbon vapor at 2000°K. 3.3×10^{-11} atm. C, 1×10^{-11} atm. C_2, and about 10^{-10} atm. C_3. Under conditions where vapor is withdrawn at an appreciable rate, C_5 is of no importance but under static conditions it may become the predominant species.

Honig (35) has observed all silicon gas species from Si through Si_7 and has obtained heats of sublimation to Si_1, Si_2, Si_3, and Si_4. Molecular species appear to total about 1 per cent of the concentration of silicon atoms. Douglas (85) has observed the Si_2 spectrum. Honig's value for the heat of sublimation of silicon to Si is considerably higher than those previously obtained, and a calculation from the D_0(SiO) of Barrow & Rowlinson (34) and from the heat of formation of SiO(g) (Brewer & Edwards (86) and Porter, Chupka, & Inghram (5)) yields a value in agreement. The higher value is probably substantially correct and should be refined by Third law evaluation of new vaporization experiments.

Honig has also detected all possible germanium and tin polymers through Ge_7 and Sn_5 and a small concentration of Pb_2 (84, 87). The total concentration of tin molecules is only of the order of 0.1 per cent that of the atoms, but the concentration of germanium molecules may be 10 per cent that of the atoms. Köhl (88) in a less detailed investigation of the polymerization in germanium vapor has obtained results that confirm the qualitative conclusions of Honig as to the species present above germanium, silicon, and tin. But Köhl's ion intensities often differ sharply from those found by Honig not only in their abundance relative to the atomic ions but relative to other molecular ions. Köhl found higher concentration of germanium and tin molecules than did Honig but found relative concentrations of silicon molecules from 1/10 to 1/100 those reported by Honig. The discrepancies may arise in part from the fact that Honig's vapors were generated under more nearly equilibrium conditions than were Köhl's. Determinations of average molecular weights of the vapors by Searcy & Freeman (89, 90) indicate that molecules constitute at most only a few per cent of either germanium or tin vapor in best agreement with the results of Honig.

Independent investigations by Ruamps (91) and by Kleman, Lindkvist & Selin (92, 93, 94) have resulted in the identification of diatomic molecules in the emission spectra of copper, silver, and gold. The latter authors have calculated approximate dissociation energies from linear extrapolations of the ground state vibrational levels. It is striking that the bond energy found for Ag_2 is less than that of either Cu_2 or Au_2 just as the lattice energy of solid silver is less than that of solid copper or gold. Ruamps (95) observed bands attributed to CuAu and Cu_nAu molecules. Studies of the bond energies and bond distances in such mixed metal molecules in comparison with molecules of the separate elements should provide extremely interesting tests of current bond theories.

Agreements between the dissociation energies calculated from spectroscopic data for the copper family diatomic molecule and unpublished mass spectroscopic values of Schissel are good. The values are too low to make diatomic molecules major species in vaporization of these elements. The concentration of molecular species in silver vapor is apparently not so high as inferred by Searcy, Freeman & Michel (96) from preliminary vapor density measurements. The high proportion of the thermal ions Ag_2^+ Ag_3^+ and Ag_4^+ that they observed relative to Ag^+ may result from the existence of a slow process in the mechanism for vaporization of silver to the monoatomic ion compared to those for vaporization to polyatomic ions.

Miller & Kusch (97) have measured by nuclear magnetic resonance the concentrations of K_2 and Tl_2 in a molecular beam. They conclude that the concentration of K_2 in a potassium beam is a little less than 0.5 per cent in agreement with earlier data by other techniques, and that Tl_2 cannot make up as much as 0.05 per cent of their thalium beam. Gauzit (98) has used an electron microscope essentially as a mass spectrometer with very high voltage to produce as gas species Li^-, and probably Na^- and K^-.

Heats of Dissociation of N_2 and CO

The heats of dissociation of the isoelectronic molecules N_2 and CO have been controversial topics for several decades. A wide variety of experiments including spectroscopic, photochemical, electron impact appearance potential, and high temperature chemical measurements have seemed irreconcilable. The resultant conflict has attracted a great deal of new experimental work, especially during the last two years. Many new types of measurements as well as re-evaluation of old measurements have yielded unambiguous values for these two quantities that are of considerable importance to many fields in addition to high temperature chemistry.

Gaydon (99) has presented a comprehensive review of data available up to early 1952. The work done since then has been so extensive that space would not be available here for a comprehensive review. The present survey will cover mainly papers published this last year with a few of the more important papers of the preceding year.

The starting points for these problems are the well-established predissociations in the CO and N_2 spectra from which maximum values of D(CO) and $D(N_2)$, the dissociation energies of CO and N_2 at 0°K., can be fixed. In addition, two or three lower values for the dissociation energies differing from the maximum values by accurately known electronic excitation energies of the atomic products are possible. This relatively simple picture had been complicated by reports of predissociations at lower energies and by suggestions that the predissociations may correspond to maxima in the CO and N_2 potential energy diagrams rather than to true dissociation limits. The existence of maxima would allow quite a range of possible dissocation energies consistent with the observed predissociations rather than a few sharply fixed values. The recent spectroscopic work of Douglas (100) and Douglas

& Møller (101) has now returned the situation to its original simplicity. Their spectral work with both $C^{12}O$ and $C^{13}O$ has repudiated the existence of any predissociations below 11.1 *ev* for CO and the existence of any appreciable maximum in the potential diagram. Gaydon & Fairbairn (102) have likewise eliminated a low predissociation reported for NO.

It is possible through thermochemical cycles to relate $D(N_2)$ to $D(N_2^+)$ and $D(NO)$. Through these relationships and measurements of high vibration levels of N_2^+ by Douglas (103) and of NO by Brook & Kaplan (104) together with the dissociation limit of NO determined by Tanaka (105), it is now possible from these spectroscopic data alone to conclude that any value of $D(N_2)$ other than 9.758 *ev* is very unlikely. However, one need not rely upon spectroscopic data alone.

Over a half-dozen different high temperature measurements of the degree of dissociation of N_2 have been reported recently. They all agree in eliminating any of the possible low values of $D(N_2)$. The measurements of Kistiakowsky, Knight, & Malin (106); Gaydon, Thomas, & Brewer (107); and those of Conway, Wilson & Grosse (108) consisted of measurement of the temperature attained in a cyanogen-oxygen flame. All investigators obtained temperatures higher by several hundred degrees than could be possible if $D(N_2)$ were 7.38 *ev*, the next possible value below 9.758 *ev*, resulting in more extensive dissociation of N_2 in the flame. Farber & Darnell (109); Toennies & Greene (110); and Christian, Duff & Yarger (111) attempted to measure directly the heat effect due to dissociation of nitrogen exposed to a hot wire in the first case and subjected to shock waves in the latter two. The most direct method was that of Hendrie (112) who examined hot nitrogen gas with a Stern-Gerlach apparatus to determine the extent of dissociation to atoms. All of the high temperature measurements are in agreement and by themselves clearly establish the high dissociation energy of nitrogen.

In the past, electron impact appearance potentials have constituted the strongest indications for $D(CO)$ less than 11.09 *ev* or 255.8 kcal., and of $D(N_2)$ less than 9.758 *ev* or 225.0 kcal. On the basis of the discovery of Branscomb & Smith (113) that the commonly accepted electron affinity of oxygen was in error by 0.8 *ev*, Hagstrum (114) has reevaluated the electron impact data for N_2, NO, and CO obtaining much better agreeement with the higher dissociation energies than with the possible lower values, although minor discrepancies exist. Kandel (115) has presented new data for N_2 in agreement with Hagstrum. Using essentially monoenergetic electrons, Burns (116) and also Clarke (117) have presented new electron impact determinations for N_2 that directly fix $D(N_2)$ at 9.76 *ev* by identifying the electronic states of the dissociation products. The only remaining electron impact work that has not been reconciled with the high dissociation energies is the hydrocarbon work of Langer, Hipple, & Stevenson (118) that indicates $D(CO) = 9.5$ *ev* if the value they have chosen for $D(CH)$ is correct.[2]

[2] T. E. Brackett [*J. Chem. Phys.*, **24**, 1103 (1956)] has suggested an explanation for the discrepancy.

Although the CO and CO^+ spectroscopic data are most easily interpreted in terms of $D(CO) = 11.09$ *ev*, one cannot, as for N_2, present unambiguous and completely convincing arguments for the high dissociation energy from spectroscopic considerations alone.

Kistiakowsky, Knight, & Malin (106) believe their data for cyanogen-oxygen explosion, which clearly establishes a high value for $D(N_2)$, also fixes $D(CO) = 11$ *ev*. Goldberg & Müller (119) have made an interesting high temperature determination of $D(CO) = 11$ *ev* from the concentrations of CO, C, and O in the sun. However, neither of these determinations by themselves would be convincing.

Through the heat of formation of CO, $D(CO)$ can be directly related to the heat of sublimation of monatomic carbon from graphite. It is toward the determination of this quantity by high temperature measurements that most recent efforts to fix $D(CO)$ have been directed. The publications of the last year have shown all high temperature investigators to be in complete agreement with $D(CO) = 11.09$ *ev* or 255.8 kcal., and $\Delta H_0^0 = 169.58$ kcal. for C(graphite) = C(g).[3]

The most important recent development has been the application of the mass spectrometer by Chupka & Inghram (3, 120, 121) and by Honig (4) to allow study of each of the carbon gaseous species independently. The Knudsen cell measurements by Inghram and Chupka clearly establish a vaporization coefficient for monatomic carbon of the order of magnitude of unity and an equilibrium heat of sublimation of around 170 kcal. in agreement with the high $D(CO)$ value. Additional total vapor pressure measurements by Hoch, Blackburn, Dingledy, & Johnston (122), Thorn & Winslow (123), and by Goldfinger (77) and mass spectroscopic Langmuir type experiments by Honig all support Inghram and Chupka's conclusions.

The situation of the dissociation energies of CO and N_2 has thus changed during the past two years from apparently irreconcilable deadlock to essentially unanimous agreement. No other problem in chemistry has, in recent years, been subjected to such a searching fundamental examination. In view of the long-standing uncertainty, only a very decisive result could be convincing. The agreement among the unprecedented number of experiments of widely differing character has provided this decisive resolution of the problem and there can no longer be any question of the values of $D(CO)$ and $D(N_2)$. The value of $D(N_2)$ expressed in various units is $78{,}717 \pm 40$ cm^{-1}, 9.758 ± 0.005 *ev*, or 225.04 ± 0.1 kcal. The value of $D(CO)$ is $89{,}460 \pm 150$ cm^{-1}, 11.090 ± 0.019 *ev*, or 255.76 ± 0.43 kcal. For the related quantities, $D(CO^+) = 8.34 \pm 0.04$ *ev* and $D(N_2^+) = 8.727 \pm 0.005$ *ev*. $D(NO) = 6.503 \pm 0.004$ *ev* or 149.98 ± 0.08 kcal. For C(graphite) = C(gas), $\Delta H_0^0 = 169.58 \pm 0.45$ kcal. and $\Delta H_{298} = 170.89 \pm 0.5$ kcal. As pointed out by Douglas & Møller (101) the uncertainty in the CO and C heats is due to lack of knowledge of which components of the C and O triplets are involved in the

[3] Use of latest values of constants and conversion factors for different units result in slightly different numbers than used in most of the references.

predissociation of CO. Thus the predissociation data yield nine possible $D(CO)$ values ranging from 89,595 to 89,325 cm^{-1}. It does not seem likely that it will be possible to narrow this range in the near future. It should be pointed out that the uncertainties listed are not probable errors as the chances of the true values being outside the ranges given are very small. The probable error (50-50 chance of being outside given range) for $D(CO)$ would be ± 92 cm^{-1} or 0.26 kcal. This causes a probable error of seven per cent in the dissociation constant of CO or vapor pressure of carbon at 2000°K.

Complex Oxide Phases

A most significant development has been a clarification of the complexity of the Ce—O system by the work of Brauer & Holtschmidt (124), Brauer & Gradinger (125), and Bevan (126) and of the Pr—O and Tb—O systems by the work of Ferguson, Guth, & Eyring (127), Guth, Holden, Baenziger, & Eyring (128), Simon & Eyring (129) and Guth & Eyring (130). The similar behavior of the systems is illustrated by Table I where the

TABLE I

O/M Ranges for Oxide Phases of Ce, Pr, and Tb

Ce	1.50–1.54 hex	1.65–1.69 cub		1.71 –1.72 rhomb	1.78 rhomb	1.80–1.81 cub	2.0 cub
Pr	1.5 –1.6 hex	1.6 –1.68 cub	1.70 cub	1.715–1.72 rhomb	1.77–1.80 rhomb	1.85 cub	2.0 cub
Tb		1.5 cub		1.71 rhomb		1.81 cub	

oxygen to metal atomic ratios and the symmetries of the known phase regions are given.

The cubic phases of lowest oxygen content have the Mn_2O_3 structure while the cubic phases of higher oxygen content have the closely related CaF_2 structure. The intermediate rhombohedral phases represent intermediate structures with slight distortion from cubic symmetry. At high enough temperatures, the oxygen partial pressure results for the Pr—O system indicate that a homogeneous phase region can be expected from $MO_{1.5}$ to MO_2 with no miscibility gaps in the transition from the Mn_2O_3 structure to the CaF_2 structure. However, the solution is not an ideal one and has a number of intermediate compositions that correspond to especially stable arrangements. Thus, as the temperature is lowered, the homogeneity range breaks up into a series of phase regions that become steadily narrower as the temperature is lowered. Because of the difficulty of attaining equilibrium at the lower temperatures, it is not possible to define the composition ranges of these phases very well and it is probable that even more of these

closely related phases will be found as conditions closer to equilibrium are reached at lower temperatures. It is interesting to note that the cubic Mn_2O_3 structure that is stable down to composition $MO_{1.5}$ at high temperatures appears not to be stable at lower temperatures except at the oxygen rich end of its homogeneity range and the hexagonal La_2O_3 type structure appears to become stable at lower temperatures around the composition $MO_{1.5}$ in the Ce and Pr systems. Tb_2O_3 has not been observed in the hexagonal form.

Another interesting illustration of immiscible oxide phases of similar structure is given by the V—O system where Andersson (131, 132) reports seven monoclinic oxides with O/V ratios 1.67, 1.75, 1.80, 1.84, 1.86, 1.87, and 2.0. He believes some of these may be designated as a V_nO_{2n-1} series. Schönberg (133) and Seybolt & Sumison (134) have also contributed to knowledge of the V—O system and twelve distinct intermediate phase regions are now established between vanadium metal and oxygen gas not counting the many V_2O_3 and VO_2 transitions listed by Jaffray & Dumas (135). Most of these are undoubtedly second-order transitions and do not correspond to phase transformations.

A rather confused situation exists at present with respect to the Ta—O system. Wasilewski (136) reports only the phase Ta_2O between Ta and Ta_2O_5 with a low and high temperature form of Ta_2O_5. Schönberg (137) however, reports Ta_4O (orthorhombic), TaO (NaCl type), TaO_2 (rutile), $TaO_{2-2.5}$, and Ta_2O_5 (orthorhombic Nb_2O_5 type). He reports that he could not prepare the high temperature form of Ta_2O_5. This is surprising since Brewer (6) in his 1952 review listed three reports of preparation of a high temperature form of Ta_2O_5. Since then, it has been shown (141) that high temperature forms of Ta_2O_5 reported by Schäfer, Dürkop & Jori (138, 139) and by Lagergren & Magneli (140) have the same structure as the earlier preparations.[4] Wasilewski (136) reports conversion of the low form of Ta_2O_5 to a high temperature form in agreement with Lagergen and Magneli. He also reports preparations of this high form by reduction of Ta_2O_5. Thus it appears very likely that Schönberg's $TaO_{2-2.5}$ is the high temperature form of Ta_2O_5 but his paper gives no details that would allow comparison.

The lower tantalum oxide phases reported by Schönberg were not prepared in the binary Ta—O systems but were prepared by oxidation of Ta metal or compounds such as hydrides, nitrides, carbides by steam in the presence of hydrogen or ammonia or by reduction of Ta_2O_5 by carbon. Under such conditions it is not improbable that traces of C, N, or H impurities stabilized phases that could not exist in the binary system; Schön-

[4] The powder diffraction lines measured by Magneli have been given in the ASTM index of x-ray diffraction patterns. There are two typographical errors. The first line should read 8.90 instead of 9.90 and the strongest d value should be 3.77 A instead of 4.77 A. The pattern was indexed as orthorhombic pseudotetragonal (142).

berg notes that most of the phases could not be prepared pure. It is also possible that the indirect methods used favored formation of phases that are metastable. On the other hand, there may be stable phases that form only with great difficulty in a binary system due to very slow rates of reaction and a round-about method would be required to produce them.

In this connection, Schönberg's (73, 143) report of ZrO is a good illustration. Schönberg (143) has confirmed the observations of Cubicciotti (144), Hoch, Nakata, & Johnston (40), Domagala & McPherson (145), Hardy & Hulm (146), and earlier workers, that no intermediate phases can be prepared from Zr and ZrO_2 at 1200–1700°C. However, by oxidation of Zr metal with steam in the presence of a great excess of hydrogen between 600°C. and 800°C. phases of NaCl type with lattice constants varying from $a = 4.584$ to 4.620 Å were produced along with ZrO_2. Vacuum heating at 1000°C. for two hours caused no structural change. Schönberg thus concludes the existence of a ZrO phase with a wide homogeneity range. The high temperature observations would seem to indicate the instability of ZrO above 1200°C. It is conceivable that ZrO becomes stable at lower temperatures but cannot be formed directly from Zr and ZrO_2 in the temperature range of stability due to slow rates of reaction. However, under such conditions, it is very unlikely that ZrO could ever have a wide homogeneity range. It must have a sharp composition at the upper temperature of its stability range and although its homogeneity range under such conditions would widen as the temperature is lowered, it is very unlikely that the homogeneity range could ever become wide enough to detect by x-ray diffraction. Thus the range of lattice constants reported indicates lack of equilibrium.

It is thus impossible from the available data to clarify the Ta—O and Zr—O systems. Much additional work will be required to clear up the questions raised by Schönberg's interesting work.

Recent work by Kihlborg & Magneli (147) and Blomberg-Hansson, Kihlborg & Sundkvist (148) on the molybdenum oxides provides another illustration of the complexity of the transition metal oxide systems. There are six phases of known structure with at least three more of unknown structure. Work with oxide systems containing both Mo and W reveals the existence of a series of oxide phases that can be represented by the formula M_nO_{3n-1} with values of n ranging from 8 to 14. The addition of tungsten increases the thermal range of stability as well as the number of these phases that are stable. Magneli & Andersson (149) have found the monoclinic MoO_2 structure for the dioxides of W, Tc, and Re. This structure is interesting in that it is a deformation of the rutile structure resulting from pairs of metal atoms tending to approach one another attributable to some electrons forming metallic bonds between cations. Hägg & Magneli (150) have recently reviewed the molybdenum and tungsten oxide system.

Further work has likewise demonstrated the uranium-oxygen system to be more complicated. Wait (151) has found a cubic $UO_{2.82}$ phase with the ReO_3 structure. Grønvold (152) and Katz (153) report new high temperature studies of the UO_2—U_3O_8 region.

Metallic Interstitial Compounds and New Ternary Systems

Over the years, the laboratory of Hägg (154) has been very active in the study of interstitial compounds of the metals. Most of the past activity was directed toward carbides, nitrides, and hydrides. Schönberg, one of the recent contributors, has published two dozen papers extending the study of interstitial compounds to oxide systems. His work on the oxide systems of Zr, V, and Ta has already been noted above. In addition, he has published work on both binary and ternary oxide, nitride, carbide, and phosphide systems.

One of the most interesting discoveries by Schönberg (155, 156, 157) has been demonstration of phases of composition $M_3'M_3''O$ and $M_2'M_4''O$ having the same structures as the cubic, high-speed steel carbides or the η_1 and η_2 carbides (158 to 161). M′ can be Mn, Fe, Co, Ni, or Cu when M″ is Ti and M′ can be Mn, Fe, Co, and Ni when M″ is Mo or W. For the first group there is complete miscibility between the η_1 and η_2 phases similar to that observed for the carbides. For the second group, only the η_1 phase with a narrow homogeneity range is observed. These phases can be formed with various proportions of the oxygen replaced by nitrogen and possibly carbon. Ta also forms similar oxides with the η-carbide structure with Mn and Fe and probably Co and Ni (162). In addition, Schönberg (155, 157) has shown the existence of oxides with an ideal composition M_2X with the oxygen in interstitial positions in a hexagonal metal lattice. By analogy with the hexagonal A3 metal structure, these phases are designated as L′3 type. They have broad homogeneity ranges extending in some instances from zero to a maximum of 33 atomic per cent oxygen. The wide homogeneity ranges for oxygen in α-titanium and α-zirconium are believed to represent such phases. In other systems, one must have a mixture of two metals as represented by $M'M''O_x$, where M″ is Fe or Co when M′ is Mo or W, and M″ is Ti, V, Cr, Mn, Fe, or Co when M′ is Re. x is usually between 0.4 and 1, although for some of the rhenium systems, x may extend to zero. These phases have metallic properties similar to those of corresponding nitrides and carbides of the transition metals and should prove to be quite useful materials. Rostoker (163) has attempted to determine the role of the ternary oxide phases in the Ti—O systems with Fe, Cr, and Ni at 900–1000°C. Phases with the cubic, high-speed steel carbide structures were found although the homogeneity ranges differed considerably. A range Ti_4Fe_2O—Ti_3Fe_3O was found in the Fe—Ti—O system while in the Ti—Cr—O system the range was narrow and near Ti_3Cr_3O at 1000°C. Wang & Grant (164) however also find a phase near Ti_4Cr_4O which may not be stable below 1200°C. Neither of these phases melts congruently. Rostoker (163) finds the binary Ti_2Ni phase takes up oxygen with approximately constant Ti/Ni ratio forming a ternary phase with the cubic η-carbide structure. Hilty, Forgeng, & Folkman (165) have also shown the importance of two ternary phases at 1550–1650°C. in the Fe—Cr—O system. One phase has the Cr_3O_4 structure with up to 8 per cent Fe replacing Cr. The other phase has a distorted spinel structure intermediate between Cr_3O_4 and FeO—Cr_2O_3.

The phases are stable only at high temperatures. Many of these phases have been overlooked in the past because of the limited temperature ranges of stability.

Another group of metallic oxides (133, 166, 167) includes Cr_3O, Mo_3O, and W_3O. It now appears that the reported cubic modification of tungsten was actually W_3O. The other two of these oxides are difficult to prepare as they appear to be unstable at very high temperatures where rates of reaction between the metal and high oxides are rapid. They have not yet been prepared as single phases. At lower temperatures, where these phases become stable, their rates of formation become so slow that they can be produced only in a narrow temperature range near the upper temperature of their stability range. In order to insure that his mixture of Mo and MoO_2 would be held in the narrow temperature range required for formation of Mo_3O, Schönberg started with a mixture at 1000°C. and lowered the temperature 10° every day. Previous heating of Mo and MoO_2 between 1100–1600°C. produced no Mo_3O indicating instability at higher temperatures.

The discovery of these various types of sub-oxides by Schönberg is one of great importance. There may be many other phases that have escaped detection in phase diagrams because their ranges of stability do not extend up to high enough temperatures to allow rapid formation of the phase or because they disproportionate upon cooling unless quenched. As another example, Bumps, Kessler, & Hansen (168) found a $TiO_{0.66-0.75}$ (tetragonal) phase in the thoroughly studied Ti—O system. This phase is stable only below 925°C. and forms only slowly at lower temperatures.

A somewhat more simple method of looking for such phases than the method used by Schönberg would be the use of a furnace with a temperature gradient extending from 1000°C. to room temperature. If a mixture of Mo and MoO_2 were spread along the furnace, one would be sure of subjecting the mixture to every temperature between 1000°C. and room temperature. Then examination of samples taken along the length of the furnace would indicate whether any new phases formed. Such a procedure would allow very long heating times and would also allow fixing of the temperature range in which these phases are formed. It is of great importance to continue the search for such phases. These phases are important not only for the unique properties that they will surely have but because knowledge of their existence is vital for the understanding of interaction of metals and oxides or of similar systems. Thus thermodynamic calculations of attack of oxides by metals cannot be reliable if such phases are not taken into account. These phases may also be important intermediates in processes such as the sealing of metals to oxides.

In addition to the metallic oxides, Schönberg (157, 162, 169) prepared a number of other ternary oxides. He found either Mo or W would replace possibly up to half of the Cr in Cr_2O_3 (corundum structure). He produced Mn_2TaO_3 (close to CoSn type) and observed a hexagonal $(Fe, W)O_2$ phase with a structure close to that of monoclinic WO_2. He was able to prepare

a series of black oxides with the cubic fluorite structure with mixtures containing Ti and either Fe, Co, or Ni or containing Zr and either V, Cr, Mo, W, or Mn. The Ti or Zr varied from 50 to 75 per cent of the metal content. V, Cr, Mn, Fe, Co, or Ni did not form oxides with fluorite structure when combined with Nb, Ta, Mo, or W. As might be expected from the great difference in electropositive character, Ti, V, and Cu could not be introduced into Cr, Mo, or W oxide phases. The first two had to be completely oxided before the sixth group metals could be oxidized while Cu could not be oxidized until the sixth group metals were completely oxidized. A study of ternary systems involving N, Ta, and various transition metals from Ti to Ni also yielded a number of interesting ternary nitrides (170).

Several interesting systems involving a metal, oxygen, and another nonmetal have been studied. Such studies are important as a number of reported binary nitrides have turned out to be oxy-nitrides. As oxygen is a common impurity, it should be considered as a component of any system under study. In a study of phosphides of Ti, Zr, V, Nb, Ta, Cr, Mo and W, Schönberg (143, 171) also observed Ti_3PO_2 and Zr_3PO_2 phases that appeared at first to have cubic NaCl structures but were found to be distorted slightly to a hexagonal symmetry. Likewise in a study of the Nb—N and Ta—N systems, a number of oxy-nitrides were encountered. It is of interest to compare the behavior of the related V, Nb, and Ta systems. All three metals dissolve up to about 2 atomic per cent nitrogen. Schönberg (172) also reports a $TaN_{0.05}$ phase in which the Ta atoms are only slightly displaced from the body-centered cubic lattice of pure Ta. However, he indicates that this phase does not have a homogeneity range extending to the metal. A similar phase has not been reported for V or Nb. All three metals have a hexagonal M_2N phase of L'3 structure. Nb and Ta but not V have a hexagonal $MN_{0.8-0.9}$ phase of MoN or WC type (173). Schönberg (174) also reports this same structure for WN, $Ti_{0.7}$(Co or Ni)$_{0.3}N$ and $Mo_{0.8}$ (Co or Ni)$_{0.2}N_{0.9}$. He confirms the previously reported $NbN_{0.95}$ (anti-NiAs) and VN(NaCl type), NbN (hexagonal γ'—MoC type), and TaN (hexagonal B35 type). Brauer & Zapp (175) agree on Ta_2N and TaN but did not find $TaN_{0.8-0.9}$ or $TaN_{0.05}$. A number of other phases have been reported for these metal-nitrogen systems. Schönberg (173, 176) finds these other phases to be ternary phases. Thus he finds $NbN_{0.9}O_{0.1}$ (cubic NaCl type), $NbN_{0.6}O_{0.3}$ (tetragonally deformed NaCl), $TaN_{0.9}O_{0.1}$ (slightly distorted hexagonal B35 type), $TaN_{0.75}O_{0.25}$ (close to hexagonal WC type), $TaN_{0.65}O_{0.35}$ (close to hexagonal WC type), and $TaN_{0.50}O_{0.50}$ (unknown structure). In addition, Schönberg (176) studied the Ta—C—N and Ta—C—O systems finding indications of complete miscibility of Ta_2N and Ta_2C. About 5 atomic per cent TaC can be dissolved in $TaN_{0.8-0.9}$ with probably fairly small solubility of TaC in TaN. The Ta—O—C system yielded Ta_2(C,O) with a tetragonally deformed NaCl structure probably similar to $NbN_{0.6}O_{0.3}$ and two phases of unknown composition. One of these was face-centered cubic with $a = 10.41$ Å. The interesting quaternary phases ZrTaNO and ZrNbNO are found to

have an ordered hexagonal close-packed metal arrangement but the nonmetals appear to behave differently than in the typical interstitial compounds (154, 73).

Schönberg (177) has restudied the Mo—N and W—N systems confirming the previously known molybdenum phases but finding only W_2N (face centered cubic) and WN (hexagonal WC type). Kiessling & Peterson (178) find that other previously reported tungsten nitrides are oxy-nitrides. Thus they find $W_{0.75}N_2O_{1-2}$ and $W_{0.62}N_{0.62}O_{0.38}$ (defective NaCl).

Other High Temperature Condensed Systems

Increasingly, high temperature processes are being used to make materials more efficiently than is possible in other ways. There is room here to discuss only a few examples of recent work.

Certainly one of the most significant scientific events of the past year has been the announcement of the successful laboratory conversion of graphite and hydrocarbons to diamond by application of high temperature and high pressure (179). The list of physical scientists who have at some time or other made an attempt, usually unpublished, to make diamonds is probably longer and more illustrious than that associated with any other chemical problem. The most important thing, however, is not that the famous problem was solved, but that the apparatus with which the problem was solved opens a pressure-temperature area for investigation that had seemed impossible to reach. The apparatus can develop 100,000 kg./cm.^{2} pressure at 3000 K. for time periods at least of the order of minutes and can be operated at 100,000 kg./cm.^{2} above 2300 K. for hours. Experiments in this new range should contribute greatly to our understanding of structures and bonding and should contribute some remarkable new materials.

Recent structural work on silica impressively illustrates some of the possibilities of temperature and pressure as tools for producing new materials and also illustrates the complexity of systems once thought to be relatively simple and completely explored. In the past two or three years, six new modifications of silica have been reported. Of these, four are distinctly new crystallographic modifications and three were produced by use of high temperature or a combination of high temperature and pressure.

Condensation of SiO with exclusion of moisture sometimes yields silicon plus a low density, water-soluble, fibrous form of silica (180, 181). At 35,000 atmospheres and 500–800 C., a high density, hydrofluoric acid-insoluble form of silica separates from certain melts (182). At 380–585 C. and 350–1250 atmospheres of water vapor a form of silica is crystallized that is similar to quartz, but of tetragonal symmetry (183). The preparation and properties of the various forms of silica have been recently reviewed by Sosman (184).

Schwarz & Baronetzky (185) have reacted $GeCl_4$ and hydrogen at 900–1000 C. to obtain a crystalline solid identified as $(GeCl)_x$. Panckhurst, Wilkins & Craighead (186) have obtained a number of silicon analogues

of organic chlorosulfides as well as a polymer $(SiSCl_2)_\alpha$ by reaction of $SiCl_4$ with H_2S at 700 to 1000 C. Feher, Kraemer & Rempe (187) report that H_2 reduction of S_2Cl_2 gases yields materials of formulas S_xCl_2 and S_xBr_2 where x varies from 2 to 5.2 for the chloride and from 2 to 4.0 for the bromide.

Reports of formation of two lower valent compounds by condensed phase reactions may be mentioned. Sokolova, Urazov & Kuznetsov (188) by thermal, x-ray, and microscopic examination of the bismuth-bismuth trichloride phase diagram established the existence of a subhalide that they designated BiCl although the composition at which the phase was observed was 58–97 atom per cent Bi. The compound is unstable at room temperature. Ehrlich and coworkers (189) have identified as CaHCl the compound previously reported to be CaCl by Ehrlich & Gentsch (190) and by Wehner (191).

If CaCl does not exist, there remains no convincing evidence for the successful preparation of a solid subhalide of any alkali or alakline earth metal. It has proved possible, however, to obtain intermediate oxidation states in fused salt-fused metal mixtures. Bredig, Johnson & Smith (192) have investigated the sodium-sodium halide systems and Bredig, Bronstein & Smith (193) have investigated the potassium-potassium fluoride and cesium-cesium halide systems. In every system studied, miscibility of the liquid metal and the liquid salt increased rapidly toward complete miscibility with increasing temperature. The greatest mutual solubility was observed for the cesium-cesium halide systems which showed complete miscibility at the melting points of the salts. Bredig and co-authors were able to correlate their data on solubilities and heats of solution of metals in molten halides with cohesive energies of the metals and salts and with the relative difficulty of substitution of ions of various volumes for the electrons of a metal lattice.

Previous papers have also presented evidence for Al^+ in cryolite and other liquid systems, and Corbett & von Winbush (194) have reported evidence for the presence of subhalides in Al—AlI_3 and Ga—$GaCl_2$ melts. Solubilities above the salt melting points were found by the latter authors for Pb, in $PbCl_2$, Tl in TlCl, Ag in AgCl, Ga in $GaCl_2$, Al in AlI_3 and Sn in $SnCl_2$ and $SnBr_2$. All solubilities were of the order of 0.01 to 0.1 mole per cent, except that the solubility of Ga in $GaCl_2$ was about 2 per cent.

Solutions of Cd in molten $CdCl_2$ which have recently been reinvestigated by Grjotheim, Grønvold, and Krogh-Moe (195) are particularly interesting because, as pointed out by those authors, considerable evidence has been accumulated for the belief that Cd dissolves by reaction to form Cd_2^{++} ions.

Further studies of lower halides of the 4th group have yielded information on TiF_3 (196), ThI_3, and $ThCl_3$, (197) and $NbCl_3$ and $NbCl_4$ (198). The $NbCl_3$ work by Schäfer (199) is especially significant as a wide homogeneity range $NbCl_{2.67-3.13}$ was demonstrated. Similar behavior will probably be found for other transition metal halides.

Edwards & Levesque (200) have investigated the Zr—O_2—H_2 ternary

diagram and presented a provisional condensed phase ternary diagram. Investigations by Candidus & Tuomi (201) and by Geller & Thurmond (202) appear to disprove previous reports of the existence of crystalline high-temperature GeO and SiO.

Recent High Temperature Thermodynamic Compilations

Among the most useful tools available to the high temperature chemist are the compilations of high temperature thermodynamic data that are made available from time to time. Often calculations can be performed by use of these data that make unnecessary the performance of days of difficult experimental work. Unfortunately because of the mistaken belief that the necessary calculations are complicated, far less use is made of the thermodynamic data than they merit. Several articles and books are now available which include helpful discussions of the use of such material. For example, Margrave (203) illustrates the use of $(F—H_{298})/T$ functions and lists compilations of high temperature thermodynamic data.

Several compilations of data on heats or free energies of reactions of high temperature interest have recently been published. Coughlin (204) has tabulated heats and free energies of formation of oxides as functions of temperature. Kelley, Todd, & King (205) have listed as functions of temperature heats and free energies of formation of a number of titanates from the elements and from the constituent oxides. Tripp & King (206) have constructed from older and less accurate data plots of free energies of formation of oxides from their elements and of some ternary oxides from the constituent oxides.

Two papers describing new methods of obtaining heats of formation of high temperature compounds should be noted. Robins & Jenkins (207) have taken advantage of the rapid rate of reaction of metals with silicon to determine the heats of formation of a number of silicides. They initiated each reaction by a thermite charge which evolved a known amount of heat. Thus the difference between the calorimetrically determined heat evolution and the heat due to the thermite charge gave them the heat of reaction. It is possible to compare their results with those given by Brewer & Krikorian (208) using an entirely different method. Brewer and Krikorian have determined the equilibrium composition triangles of a number of ternary systems. From the equilibrium conditions, they have set limits to the heats of formation of the silicides. The heats of formation of the silicides listed by Robins and Jenkins fall in or close to the ranges given by Brewer and Krikorian except for the zirconium silicides. The excess of silicon observed in the final samples of Robins and Jenkins indicates that their zirconium silicide heats should be somewhat more negative due to incomplete reaction. On the other hand, the zirconium silicide heats given by Brewer and Krikorian are much too negative due to a misinterpretation of their results for the Zr—O—Si phase diagram. From the observation that silicon reacted with ZrO_2 to form $ZrSi_2$, they concluded that silicon and ZrO_2 could not

co-exist and thus they drew joins between $ZrSi_2$ and SiO_2. However, calculation of the SiO partial pressure under their conditions indicates that they must have observed attack of ZrO_2 by Si due to escape of SiO gas and that ZrO_2 and Si must be able to coexist if gas cannot escape. The best set of ΔH values is probably the following: $1/2ZrSi_2$, -19; ZrSi, -37; $1/5\ Zr_6Si_5$, -41; $1/2Zr_3Si_2$, -46; $1/3Zr_3Si_2$, -46; Zr_2Si, -50; and Zr_4Si, -52 kcal. per gram atom of silicon.

Brewer has listed dissociation energies of some common molecules (209) and heats of sublimation of the elements (210). Stull and Sinke (211) tabulate heats of transition, heat capacities and entropies of the elements between 298.15 and 3000 K. A revision of this work is in progress. Free energy functions for the elements are tabulated by Brewer (212), Katz & Margrave (213) and Margrave (214). Heat and entropy data for some common gases and graphite between 3000 K. and 12000 K. have been calculated by Fickett & Cowan (215). Hultgren & Orr (216) are in the process of preparing a critical review of the thermodynamic data available for all metals and binary alloys. Sections of this work are available in loose leaf form as they are completed.

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THERMOCHEMISTRY AND THERMODYNAMICS OF SUBSTANCES[1]

By Charles W. Beckett, Melville S. Green and Harold W. Woolley

Thermodynamics Section, Division of Heat and Power, National Bureau of Standards, Washington, D.C.

DEVELOPMENTS IN THE EQUATION OF STATE AT VERY HIGH PRESSURES AND TEMPERATURES

In recent years interest in the thermodynamic properties of substances at very high temperatures and pressures has increased. For our present purposes, we may define high temperatures and high pressures to be conditions under which any material of which an experimental apparatus might be made cannot long maintain its integrity, i.e., $T > 3000°C.$ and $P > 2 \times 10^5$ atm. Such temperatures and pressures have long been of interest in geophysical (19, 50, 114 to 116) and astrophysical (7, 117 to 119) applications. More recently, these conditions have been attained and measured in transient experiments. Since the experimental techniques are so difficult, a large role has necessarily been played by theoretical calculations. The present article will be divided into three main sections. The first will be devoted to the so-called Thomas-Fermi method which is most appropriate to matter at high densities, the second to a discussion of recent experimental developments, and the third to theoretical methods, most appropriate at low densities, which treat matter as a mixture of chemically reacting ideal gases.

In a still very illuminating review of this subject written in 1936 Hund (124) has shown how the variation of the density of matter over a very wide range of temperature and pressure can be sketched from simple quantum and statistical mechanical ideas.

At sufficiently low temperatures and laboratory pressures, the thermodynamically stable state for all substances is a condensed phase, either liquid or solid, with a density which is nearly independent of temperature and pressure, but highly dependent on position in the periodic table. The binding energy per atom corresponds to temperatures varying from tens and hundreds of degrees for molecular crystals to several thousands of degrees for ionic or valence crystals; the atomic volumes of elements vary tenfold from transition elements to the alkali metals (and crystalline rare gases) which are the largest. As the temperature is increased at a fixed pressure of say one atm. the condensed phase becomes unstable against a gaseous phase which may consist entirely of atoms or more frequently atoms bound together by chemical valence forces into molecules. At temperatures of perhaps $2 \times 10^4°K.$ all effects of chemical binding have disappeared. Above $2 \times 10^4°K.$, ionization becomes increasingly important up to about $10^6°K.$ when all of the electrons

[1] The survey of the literature pertaining to this review was concluded in January, 1956.

have been stripped from the atoms and matter consists of a mixture of electrons and nuclei with a Maxwellian velocity distribution. The temperatures of dissociation and ionization increase rather slowly with increasing pressure. At very high temperatures the radiation pressure must also be taken into account (e.g., it is 600 atm. at 10^8 degrees and increases as T^4).

If, on the other hand, we increase the pressure at a constant temperature of say 300°K., the density of the condensed phase varies very slowly at first, changing by a factor of perhaps 2 or 3 for a pressure change from 1 to 10^5 atm. This size stability is a consequence of the Pauli exclusion principle which prevents more than double occupancy of any orbital. Eventually the the orbitals break down and the electrons behave like an ideal, degenerate Fermi gas at pressures above 10^6 atm. As the pressure is further increased, the velocity of the electrons increases until at about 10^{18} atm. the electrons have relativistic velocities. Above 10^{23} atm. the nuclei are no longer stable.

The transition from the condensed phase to the degenerate Fermi gas can be understood as a pressure ionization [Kothari (7, 8), Michels *et al.* (122), and de Groot & Ten Seldam (112, 126)]. As the density is increased the outer orbitals become distorted and ionization potentials vanish. The electrons in these orbitals then may be considered a degenerate gas of free electrons. At higher and higher densities, more and more bound electrons are freed from the ionic core.

Quantum Statistical Mechanics and the Thomas-Fermi Method

At the temperatures and pressures of the most usual physical-chemical interest it is possible to divide the theory of matter into two parts, a quantum mechanical theory of the aggregation of electrons and nuclei into atoms, ions, and molecules, and a statistical mechanical theory in which the properties and interactions of these entities are used to compute the properties of bulk matter. At the high temperatures and pressures, which are our primary concern here, this division is no longer sharp and we have, rather, to consider a quantum statistical theory of electrons and nuclei. It is not feasible to set up a theory which rigorously takes into account all interactions. There is, however, a method which has been used with considerable success in the quantum theory of atoms and molecules, the Hartree-Fock self-consistent field method [Fock (4)] which can be generalized to include statistical mechanical effects [Sakai (26), Husimi (23), MacDonald & Richardson (24)]. This method can be considered to be the logical basis of the more approximate, but more feasible Thomas-Fermi method which will be described in detail below.

Since the nuclei are so much heavier than the electrons we may, as in molecular quantum mechanics, neglect the motion of the nuclei in the first approximation. We imagine these to be fixed on the vertices of a lattice, or distributed in some other spatially uniform way. We seek the best (in a sense to be described below) orthonormal system of single particle wave functions (orbitals), $\psi_n(x)$, $n = 1,2,3, \ldots$, where x is the position of an electron,

$$\int \bar{\psi}_m(x)\psi_n(x)dx = \delta_{mn}, \qquad 1.$$

and where the best average frequencies of occupation of these wave functions are ρ_n. ρ_n may have any value varying from 0 to 2 corresponding to the fact that an orbital may be occupied at most twice by electrons of opposite spin. The very fact that we speak of single particle orbitals implies, of course, that we approximate the total wave function of all the electrons at any one time as an appropriate product of the functions ψ_n, anti-symmetrized to take account of the Pauli exclusion principle.

The Hamiltonian operator of a system of electrons in interaction with nuclei can be written

$$H = \sum_{i=1}^{N} H_1(i) + \frac{1}{2}\sum_{\substack{i,j=1 \\ i\neq j}}^{N} H_2(i,j). \qquad 2.$$

H_1 (1) represents the kinetic energy of each electron and its Coulomb attraction to the nuclei while H_2 (1, 2) represents the Coulomb repulsion between electrons. Assuming that the occupation numbers of different states are statistically independent, the average value of the energy can be written

$$\begin{aligned}\langle H\rangle = &\sum_{m=1}^{\infty}\rho_m \int \bar{\psi}_m(x_1)H_1(x_1)\psi_m(x_1)dx_1 \\ &+ \frac{1}{2}\sum_{m,n=1}^{\infty}\rho_m\rho_n\left\{\int \bar{\psi}_m(x_1)\bar{\psi}_n(x_2)H_2(1,2)\psi_m(x_1)\psi_n(x_2)dx_1dx_2\right. \qquad 3. \\ &\left. - \frac{1}{4}\int \bar{\psi}_m(x_1)\bar{\psi}_n(x_2)H_2(1,2)\psi_m(x_2)\psi_n(x_1)dx_1dx_2\right\}.\end{aligned}$$

The first term represents the proper energy of the electrons, the second the Coulomb interaction and the third, the exchange interaction. The factor 1/4 comes from the fact that only electrons of the same spin give rise to an exchange interaction.

The average number of electrons may be written

$$\langle N\rangle = \sum_{m=1}^{\infty}\rho_m. \qquad 4.$$

Now Gibbs has demonstrated that the expression

$$S = -k\int \rho \log \rho d\Omega, \qquad 5.$$

where ρ is the probability distribution and $d\Omega$, a volume element of phase space (k = Boltzmann's constant), attains its maximum value for given mean energy and number of particles for the canonical distribution,

$$\rho = \exp\frac{A-H}{kT}.$$

For a canonical distribution S is equal to the entropy. It can be shown that

the quantum analogue of equation 5 for an antisymmetrized product wave function is

$$S = -k\sum_{m=1}^{\infty}\left\{[2-\rho_m]\log\left(1-\frac{\rho_m}{2}\right)+\rho_m\log\frac{\rho_m}{2}\right\}. \qquad 6.$$

MacDonald and Richardson's procedure can be considered equivalent to seeking the occupation numbers ρ_m and the wave functions $\psi_m(x)$ which give the maximum value to S (equation 6) subject to the conditions that the average energy (equation 3) and the average number (equation 4) are kept constant and that orthonormality (equation 1) is maintained. The equations that ρ_m and ψ_m (X) must satisfy are

$$\left\{H_1(1)+\int dx_2\sum_n \rho_n\bar{\psi}_n(x_2)H_2(1,2)\psi_n(x_2)\right\}\psi_m(x_1) - \frac{1}{4}\int dx_2\psi_m(x_2)\sum_n \rho_n\bar{\psi}_n(x_2)H_2(1,2)\psi_n(x_1) = \epsilon_m\psi_m(x_1), \qquad 7.$$

and

$$\rho_m = 2[\exp\beta(\epsilon_m-\mu)+1]^{-1} \qquad 8.$$

where β, μ, ϵ_m are constants to be adjusted to satisfy the subsidiary conditions, equations (1, 3, 4). It may be shown that $\beta = 1/kT$, (T = temperature) and μ = chemical potential per electron. (As Brachman (33) has shown, however, μ is not the Gibbs function per electron.) The operator on the left-hand side of equation (7) which we will call H_A consists of three parts: (*a*) the proper energy of an electron, which comprises its kinetic energy and its potential energy in the field of nuclei, (*b*) the change of Coulomb energy, and (*c*) the change of exchange energy attendant on the addition of an electron to the system. The eigenvalue ϵ_m can be interpreted as the total change in energy attendant on the addition of an electron in the orbital ψ_m. Equations (7) and (8) can be considered to be the temperature-dependent generalization of the Hartree-Fock self-consistent field equations [Fock (4)] and indeed reduce to these equations when $T=0$.

Assuming that equations (7) and (8) have been solved in a mutually consistent way, we may suppose that S and $\langle H\rangle$ calculated through equations (3) and (6) are approximations to the true electronic entropy and energy of the system. It is actually more convenient to compute the Helmholtz free energy

$$A = \langle H\rangle - TS = \mu\langle N\rangle - \frac{2}{\beta}\sum_{m=1}^{\infty}\log\left[1+\exp\left(-\beta(\epsilon_m-\mu)\right)\right] - \frac{1}{2}\sum_{m,n=1}^{\infty}\rho_m\rho_n\Big[\int\bar{\psi}_m(x_1)\bar{\psi}_n(x_2)H_2(1,2)\psi_m(x_1)\psi_m(x_2)dx_1dx_2 - \frac{1}{4}\int\bar{\psi}_m(x_1)\bar{\psi}_n(x_2)H_2(1,2)\psi_m(x_2)\psi_n(x_1)dx_1dx_2\Big]. \qquad 9.$$

All other thermodynamic variables may be obtained from this potential by well known formulas. At zero temperature, equation (8) reduces to the

statement that the occupation numbers ρ_m are 2 if $\epsilon_m < \mu$ and are zero otherwise, and equation (9) reduces to the ordinary Hartree-Fock equation.

In addition to the electronic contributions to the thermodynamic functions, there are contributions from the nuclei. These may often be taken to be those corresponding to some simple model such as a perfect gas or an assembly of harmonic oscillators.

The generalized Hartree-Fock procedure outlined above has not been carried out in full detail. However, the Thomas-Fermi method which is an approximation to the above scheme has been used extensively to determine the equation of state at zero temperature and high pressures and more recently at high temperatures. Originally developed by Thomas (3) and Fermi (2) to determine electron distributions in atoms, it has since been used in a wide variety of problems in the quantum mechanics of matter (9).

Dirac (5) has shown that the Thomas-Fermi method is the semi-classical approximation to the Hartree-Fock self-consistent field method [Fock (4)]. Although the Heisenberg uncertainty principle makes it impossible to define a rigorous joint distribution for the position and momentum of a particle, it is nevertheless possible to define an approximate distribution function which is very good for wave functions of high quantum number and a large number of nodes and which is often surprisingly good even for wave functions of few nodes. Wigner (98) has made this idea of Dirac's more precise by showing how to construct a function $n_m(p,x)$

$$n_m(p, x) = \frac{1}{(\pi\hbar)^3}\int \bar{\psi}_m(x + y)\psi_m(x - y) \exp(2ip \cdot y/\hbar)dy \qquad 10.$$

which is the semiclassical distribution function corresponding to the wave function $\psi_m(x)$.

Assuming that the semiclassical approximation is valid for the most significant of the wave functions ψ_m, we may construct a function

$$n(p, x) = \sum_{m=1}^{\infty} \rho_m n_m(p, x) \qquad 11.$$

which describes the distribution in position and momentum of all the electrons in the system. In the same approximation, H_A can be expressed as a function of position and momentum

$$H_A(p, x) = \frac{p^2}{2m} - \sum_k \frac{Z_k e^2}{|x - x_k|} + \int \frac{e^2}{|x - x'|} n(x')dx' - 4e^2\hbar^2 \int \frac{(np', x)}{|p - p'|^2}dp' \qquad 12.$$

where x_k represents the position of the kth nucleus and $n(x) = \int n(p, x)dp$ is the spatial distribution of electrons. Equation (9) then becomes

$$n(p, x) = 2h^{-3}(\exp \beta(H_A - \mu) + 1)^{-1}. \qquad 13.$$

Equations (12) and (13) together constitute a nonlinear integral equation for $n(p, x)$. (Equations (12) and (13) were derived and a few solutions given by Askin and Cowan. See Latter (36) Appendix I.)

In this theory the expression (equation 9) for the Helmholtz free energy becomes

$$A = \mu\langle N\rangle - \frac{2}{\beta h^3}\int \log\left[1 + \exp\left(-\beta(H_A - \mu)\right)\right]dpdx - \frac{e^2}{2}\left[\int \frac{n(x)n(x')}{|x - x'|}\,dxdx' - 4h^2\int \frac{n(p,x)n(p',x)}{|p - p'|^2}\,dpdp'dx\right]. \tag{14.}$$

The second term can be transformed by partial integration to give the expression

$$-\frac{1}{3\beta h^3}\int n(p,x)p\cdot\nabla_p H_A(p,x)dpdx. \tag{14a.}$$

In addition to equation (14) which is a purely thermodynamic relation, there is another very useful theorem which depends on the fact that the force law between particles is of the $1/r$ type. This is the virial theorem of the Thomas-Fermi method whose derivation has been discussed by a number of authors [Fock (14), Jensen (15), Duffin (16), March (17), Brachman (18), Feynman *et al.* (31)]. This theorem states that

Pressure × volume = 2/3 kinetic energy + 1/2 potential energy + 1/2 exchange energy.

Equations (12) and (13) take into account both the effects of nonzero temperature and of exchange, but have been little used in actual computation (36). We use them here as an introduction to several modifications which have been used extensively in investigations of equations of state and other thermodynamic properties. On the one hand the case of zero temperature has been considered both with and without the effects of exchange while the case of nonzero temperature has been considered without the effects of exchange. The fourth case including both the effects of nonzero temperature and exchange has not been much considered because, according to Pines as quoted by Latter (36), at moderate temperatures, the interaction effect between nonzero temperature and exchange is cancelled by the effect of the deviation of the electronic wave function from an antisymmetrized product while at high temperature the effect of exchange is negligible.

In case the effects of exchange are neglected, $H_A(p,x)$ may be written

$$H_A(p,x) = \frac{p^2}{2m} - eV(x) \tag{15.}$$

where $V(x)$ is the electrostatic potential of the electronic and nuclear charges. The spatial density of the electrons can then be computed from the formula

$$n(x) = \frac{2}{h^3}\int\left[\exp\beta\left(\frac{p^2}{2m} - eV(x) - \mu\right) + 1\right]^{-1}dp. \tag{16.}$$

This quantity is a function of the combination

$$\bar{\mu}(x) = \mu + eV(x). \tag{17.}$$

Because $V(x)$ is the electrostatic potential of all the charges, $\bar{\mu}(x)$ in its turn satisfies the Poisson equation

$$\nabla^2\bar{\mu}(x) = 4\pi e^2 n(x) \qquad 18a.$$

with the boundary condition

$$\bar{\mu}(x) \sim \frac{Z_k e^2}{|x - x_k|} \qquad 18b.$$

in the neighborhood of nucleus k. Equations (16) and (18a) can be combined to give an equation often called the FMT equation [Feynman *et al.* (31)] which, together with the boundary conditions at each nucleus, determines $\bar{\mu}(x)$ and thereby all relevant quantities of the theory.

$$\nabla^2\bar{\mu}(x) = \frac{8\pi e^2}{h^3}\int\left[\exp\beta\left(\frac{p^2}{2m} - \bar{\mu}(x)\right) + 1\right]^{-1} dp. \qquad 19.$$

In the zero-temperature case, equation (16) reduces to

$$n(x) = \frac{8\pi}{3h^3}(2m\bar{\mu}(x))^{3/2} \qquad 20.$$

and equation (19) to

$$\nabla^2\bar{\mu}(x) = \frac{32\pi^2 e^2}{3h^3}(2m\bar{\mu}(x))^{3/2}. \qquad 21.$$

Equation (21) is the most familiar form of the equation of the Thomas-Fermi or TF theory. The case of zero temperature with exchange can also be reduced to a differential equation, the Thomas-Fermi-Dirac or TFD equation, the explicit form and the derivation of which may be found in the original papers of Dirac (5) and Jensen (125) and in the book of Gombas (9).

The earliest applications [Lennard-Jones & Woods (6), Slater (10), Slater & Krutter (11)] of the Thomas-Fermi method to equation-of-state problems were attempts to explain the properties of metals. The most rigorous way in which the Thomas-Fermi method can be applied to metals is to assume that the nuclei are situated at the vertices of an appropriate lattice (usually close packed), and to seek a solution of the Thomas-Fermi equation which has the periodicity of the lattice and which satisfies the boundary condition (equation (18b)) at the position of each nuclei. Following an idea which Wigner & Seitz (12) had used in the determination of the wave function of the free electrons in a metal, Slater and Krutter observed that the volume occupied by a close packed lattice can be divided up into equal highly symmetric dodecahedrons surrounding each vertex of the lattice, on the surface of which the conditions of periodicity require that the normal component of the electric field vanish. Within each dodecahedron, the solution has such a high symmetry that it is a reasonable approximation to suppose that $\bar{\mu}(r)$ is a function only of the distance r to the nucleus. Following Wigner and Seitz, Slater and Krutter replaced the dodecahedron by a sphere of equal volume and the conditions of periodicity by the condition

$$d\bar{\mu}(r)/dr = 0 \qquad 22.$$

on the surface of the sphere. All subsequent applications of the Thomas-Fermi method to the equation of state use this boundary condition.

Slater and Krutter computed a number of solutions of the zero-temperature Thomas-Fermi equation, both without and with exchange, in order to obtain the binding energy and other properties of metals. The virial theorem can be used to derive the simple result that the pressure is that of a Fermi gas at a density equal to that at the surface of the sphere. Since this can never be zero or negative, the TF method is unable to explain metallic binding which was one of the main objects of Slater and Krutter's investigation. The TFD method is more promising in view of the attractive exchange energy. They did indeed find a lower energy, but for copper, which was the case they considered, they found no minimum up to the largest volume for which they computed. They ascribed this failure partly to the neglect of the correlation energy which Wigner & Seitz (12) found to be a large negative contribution.

Recently March (17) has shown that there must necessarily be a solution of the TFD equations which yields a minimum energy. For copper, this minimum appears at a larger atomic volume than any used in Slater and Krutter's calculations. Since neither the TF nor the TFD methods are capable of describing adequately the periodic properties of the elements, the minimum can explain the cohesion of but one column of the periodic table. Since only in the alkali metals are the valence electrons substantially free, March applied the TFD method to these elements. Using solutions computed by Jensen *et al.* (20), and by himself, he calculated the lattice constants for the alkali metals to within 10 per cent of the observed values. The calculated compressibilities, however, are off by as much as a factor of 10.

As Slater and Krutter point out, the most appropriate application of the TFD method to the equation of state is to the very high pressure region where all periodic effects vanish. On the basis of solutions of the TFD equation for $Z=18$ and 54 Jensen (20) computed the density as a function of pressure. This was compared with experimental data of Bridgman (44, 120, 121) for La, Ba, and Cs ($Z=55$, 56, 57) at pressures up to 5×10^4 atm. At the highest pressures, the experimental densities show a tendency to converge towards the theoretical curve which Jensen takes to be confirmation of the theory. He suggests that an interpolation between the Bridgman experimental data and the theoretical curve will give an equation of state valid to within 10 per cent in a region of great geophysical interest. [Other authors do not consider this interpolation satisfactory; see for example, Bullen (19)].

A number of solutions of the TF equation have been published by Feynman *et al.*, and of the TFD equation by Metropolis & Reitz (21). A very extensive tabulation of the zero-temperature equation of state and internal energy has been given by Latter for both the TF (40) and the TFD (41) cases. March (22) has given analytical forms for the TF and TFD equations of state valid at very high pressures.

The solutions of equation (19) under boundary conditions (18b) and (22)

are of two types, those for which $\bar{\mu}(x)$ is positive throughout the sphere, and those for which $\bar{\mu}(x)$ is negative on the boundary and for some distance into the interior. ($\bar{\mu}(x)$ must always be positive near the center of the sphere because of the boundary condition (18b).) Let us consider a family of solutions of equation (19) for a fixed temperature and for increasing values of the volume of the sphere. At very small volumes, the electron density is so high throughout the sphere that $\bar{\mu}(x)$ is always large and positive. There is very little deviation from the zero-temperature case. As the volume is increased, the density and $\bar{\mu}(x)$ decrease throughout the sphere. Deviations from the zero-temperature case begin at the surface of the sphere because the density is lowest there. As long as $\bar{\mu}(x)$ is not large and negative compared to kT, solutions of equation (19) can be obtained by a perturbation procedure first proposed by Marshak & Bethe (25). In this case equation (20) can be written approximately as

$$\nabla^2\bar{\mu} = \frac{32\pi^2e^3}{3}\left(\frac{2m\mu}{h^2}\right)^{3/2}\left(1 + \frac{\pi^2}{8\beta^2\bar{\mu}^2}\right). \qquad 23.$$

The first term on the right corresponds to the zero-temperature TF equation. The second term may be treated as a perturbation starting from solutions of the zero temperature. A number of solutions of equation (23) have been obtained by Feynman *et al.* (31). The most extensive set of solutions of the perturbation equations has been given by Gilvarry (27) and Gilvarry & Peebles (28). Yokota (30) and Umeda & Tomishima (29) have presented perturbation theories which take exchange effects into account. March (38) has extended his analytic equation of state to include the effects of nonzero temperature by perturbation methods.

If we carry our family of solutions to larger volumes, the distribution of electrons at the surface of the sphere becomes completely Maxwellian. The solutions are quite unrelated to the zero-temperature solutions and must be determined by numerical methods. Along with this difference in the mathematical character of the solutions, there is a difference in the physical state represented. The situation is no longer comparable to a highly compressed condensed phase but rather to a gas consisting of ions in equilibrium with electrons.

The first numerical solutions of the FMT equation were obtained by Feynman *et al.* (31). A very complete tabulation of equation of state and internal energy based on solutions of the FMT equation has been given by Latter (42) in graphical form. It can be shown that universal curves valid for all values of the atomic number Z can be obtained by plotting $p/Z^{10/3}$ and $E/Z^{7/3}$ against ZV and $kT/Z^{4/3}$ where E is the energy per atom and V is the atomic volume. Latter gives such plots over a range of ZV from 10^{-28} cm.^{3} to 10^{-19} cm.^{3} and of $kT/Z^{4/3}$ from 10^{-4} electron volts to 8×10^4 electron volts. Latter (41) also gives plots of the zero-temperature TFD equation of state over approximately the same range of temperature and pressure and for atomic numbers from 1 to 96.

As we have emphasized above, any variation of the Fermi-Thomas method smooths out the shell structure of the electronic distribution. Since in the computation of certain nonthermodynamic properties such as opacity this structure is very important, a number of authors (34, 37, 39) have developed theories of matter at high pressures which divide the electrons into bound, which are treated by the method of individual orbitals, and unbound electrons, which are treated by equation (10).

Brachman (32) has derived expressions for the thermodynamic functions according to the FMT method by a direct integration of the Gibbs-Helmholtz equation. Latter (36) has shown how these formulas may be derived by a direct evaluation of the partition function. Brachman's formulas may also be derived from equation (14) by neglecting exchange effects and noting that in this case formula (14a) is equal to $-2/3$ kinetic energy. Gilvarry (35) has given forms of the thermodynamic functions appropriate to the perturbation method.

In accord with the definition of high pressure and high temperature given in the introduction it is very difficult to obtain experimental confirmation of the Thomas-Fermi equation of state. High pressures and temperatures certainly exist in the interior of the sun, stars, and planets and a number of applications of Thomas-Fermi methods to the theory of these bodies have been made (Brown (118), Scholte (119), Sommerfeld (117), Kothari (7), Birch (50), Kuiper (116)). In these investigations there is always a long chain of not unambiguous reasoning between the equation of state and the actual experimental observations; hence they do not provide much confirmation of the theory. Pressures which come within an order of magnitude of the pressures at which the zero-temperature Thomas-Fermi method should be applicable have been attained by static and dynamic methods to be described below. The static measurements have reached 10^5 atm. while the dynamic measurements have reached 5×10^5 atm. It is felt, however, that the Thomas-Fermi method cannot become valid below 10^6 atmospheres at ordinary temperatures (i.e., below 1000°K.). It was originally proposed by Jensen (1) and recently reiterated by Elsasser (115) that the region between available experimental observations and the domain of validity of Thomas-Fermi theory might be interpolated to within an accuracy of 15 to 20 per cent [but see Bullen (19)]. Fig. 1 shows both static and dynamic measurements on aluminum, copper, and zinc and static measurements on the alkali metals compared in each case with the appropriate Thomas-Fermi curve for each element. The alkali metals are included because of March's suggestion (13) that the Thomas-Fermi method might be valid for those elements even at zero pressure.

Static and Dynamic High Pressure Compression Measurements

Temperature and pressure ranges for static measurement of properties are limited by the strength and stability of available structural materials. Bridgman (44, 120, 121) has explored the upper pressure region near room

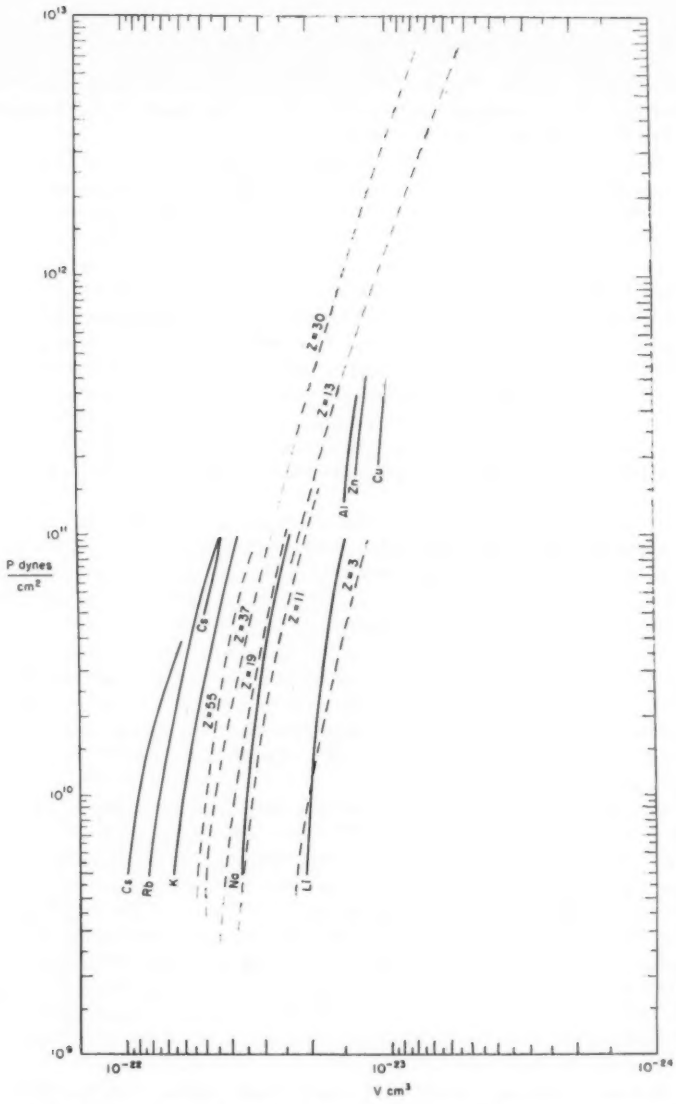

FIG. 1. The experimentally observed equations of state of number of metals compared with the Thomas-Fermi-Dirac theory. Experimental curves are full lines, theoretical curves are dashed. The experimental curves for Cs($Z=55$), Rb($Z=37$), K($Z=19$), Na($Z=11$), Li($Z=3$), are after Bridgman (44) by static methods, for Al($Z=13$), Cu($Z=29$), Zn($Z=30$), after Walsh and Christian (54) by shock methods. The theoretical curves are after Latter (36, 40, 41, 42, 45). The curves for $Z=29$ and $Z=30$ are almost coincident.

temperature. Current trends are toward much higher or much lower temperatures. Both extensions are important for a more complete understanding of the theory of the equation of state.

Hall (46) has measured the melting point of germanium as a function of pressure to 180,000 atm. He finds that the melting point decreases linearly from 936°C. with a slope of $-(3.27 \pm 0.07) \times 10^{-3}$ deg./atm. In a brief discussion of the experimental procedure, he states that the germanium sample, 2.25 mm. diameter and 7.5 mm. long, is contained in a small graphite cylinder with graphite end plugs, which also serves as an electrical resistance heating element. A thermocouple (Pt—Pt 10 per cent Rh) embedded in the graphite measured the temperature. The calibration of the latter was assumed to be independent of pressure because this type of thermocouple agreed quite well with chromel-alumel thermocouples under the same conditions. He suggests that the melting point of germanium can be used as a secondary pressure standard and as a means of determining the ultimate capabilities of a new design of an apparatus for high-temperature, high-pressure measurements.

Stewart & Swenson (47, 48, 49) have adapted one of Bridgman's methods for measuring solid compressibilities to low-temperature (4° and 77°K.) use. At pressures above 150 atm. at 4°K., no liquids exist; hence, the usual technique of embedding the solid sample in a pressure-transmitting liquid cannot be used. Instead, it is necessary to use solid materials to transmit pressures as Bridgman has done in the 100,000 kg./cm.^{2} region at room temperature. Alkali metals and some of the solidified gases (H_2, D_2, Ne, and N_2, but not A or Kr) were found to be sufficiently plastic at 4°K. to permit compressibility measurements with a simple cylinder and piston in a press designed to minimize heat exchange. Data are given also at 77°K., and for argon at 65°K.

The data, accurate to about 5 per cent, were correlated using a two constant equation derived by Birch (50) from Murnaghan's theory of finite strain (123). The experimental compressibilities are in excellent agreement with a theoretical calculation by Henkel (51, 52) for argon and by Brooks (53) for the alkali metals. The condensed rare gases and the alkali metals, since they represent, respectively, the simplest dielectric solids and the simplest of metals, are substances which are of the greatest theoretical interest. At the highest pressures attained, internuclear distances are reduced only about five per cent. However, it seems reasonable to expect that much higher pressures may be attained in the future at both low and high temperatures.

Recently published shock wave studies have yielded data on the compressibility of several metals (aluminum, copper, zinc, steel, and cadmium) and gases (argon, nitrogen, and air) at pressures or temperatures beyond the region accessible to static experimental measurement. The method consists of the production of a plane compression wave in a material which is initially at rest. The initial pressure, temperature, density, and composition

are known. The final conditions are determined by the measurement of two properties at a distance behind the shock front sufficient to allow the substance to approach closely to equilibrium at the increased pressure, density, and temperature conditions in this region. Usually, the shock velocity and either the material velocity, density, or the pressure are chosen for measurement. Reflected shock velocity may be used in conjunction with the primary shock velocity. Temperature measurement is not considered to be convenient or reliable in the short time intervals which are involved.

Basic conservation equations for mass, momentum, and energy are used to reduce the data. The results are compared with a calculated Hugoniot curve, the pressure ratio being given as a function of the density or volume ratio. This Hugoniot curve may be related to an isotherm or an adiabatic compression curve in the p.v. plane by the introduction of other thermodynamic data.

In the ballistic method, typical pressures in the explosive and metal are from 100 to 500 kilobars (10^9 dynes/cm.^{2}). The temperature rises about 200 to 500°C. in the metal. The adjacent gas shock pressures are lower, 100 to 1000 bars, but temperatures rise much higher, 6000 to 15,000°C., due to the greater entropy change in the shock compression of gases. Both shock and material velocities of the metal or gas are determined in the ballistic method by the measurement of the displacement of the plate subjected to a high-explosive plane wave. These surfaces consist of the free surface of the plate normal to the direction of the wave and other surfaces, either steps or tapered grooves machined into the plate. The displacements are measured either by high-speed photographic measurement of light produced in the shock gas at the surface, or by oscilloscopic measurement of electrical contact times of groups of contact pins of different lengths which touch the moving surfaces at different times. The measuring interval is about one microsecond (0.2 to 3 μ sec. for a representative shock wave in a gas with a final temperature of 9000°K.). Thus the rates of the various processes must be very fast if thermodynamic equilibrium is to be a valid assumption in the treatment of the data.

Hugoniot compression data are given for the following metals: Al, Cu, and Zn, by Walsh & Christian (54), Al, by Mallory (55), and Al, Cd, and steel, by Goranson *et al.* (56). The corresponding isotherms of Walsh & Christian were compared by Duvall & Zwolinski (57, 58) with several equations of state and with Bridgman's (44, 120, 121) data at lower pressures. In both metals and gases, equilibrium must be approached closely in less than a microsecond, if the high explosive method is to yield thermodynamic data. The agreement between the observations and the various equations of state tends to indicate that the relaxation times under these conditions of very high compression are sufficiently short to warrant the equilibrium assumption.

Shock data of Christian & Yarger (59) on argon and of Christian, Duff, & Yarger (60) on nitrogen were compared with the calculated Hugoniot. The

agreement of nitrogen data at high compression with the calculated Hugoniot obtained with a dissociation energy of 9.7 e.v., is regarded as strong evidence for the value 9.7 instead of 7.4 e.v. Furthermore, since the 9.7 e.v. value is now quite generally accepted,[2] the agreement throughout the experimental range which corresponds to temperatures from 8000° to 13,000°K. may be taken as evidence that thermodynamic equilibrium is approached closely in times much less than a microsecond.

In a shock tube, an approximately plane shock wave is produced in a gas by the bursting of a diaphragm by a driver gas which usually consists of a combustible mixture of hydrogen and oxygen diluted with helium. A number of different gas properties can be investigated for times up to several hundred microseconds at temperatures from about 2000° to 15,000°K. The ionization of argon was studied by Resler, Lin, & Kantrowitz (61). They obtained satisfactory agreement between measured and calculated properties. Toennies & Greene (62) recently have reported results for nitrogen which are compared with values computed using 9.7 and 7.4 e.v. for the dissociation energy. Agreement is better with the former than the latter in accordance with other recent studies. Resler (63) has obtained preliminary results with air at a low density and temperatures from 3000° to 7000°K. which agree satisfactorily with new calculated properties of air (111).

In this, as in other dynamic methods, the interpretation of the results for any particular measurement requires a careful consideration of many rate processes to establish the validity of the equilibrium assumption. The method, however, is sufficiently versatile that both equilibrium thermodynamic and rate processes may be studied in the same apparatus (64 to 69). The work of Schall (70) and also that of Dapoigny *et al.* (71) on the equation of state of water by shock compression should be noted. Finally, one should mention a quite interesting communication by Bergeon *et al.* (72) on the results of measurements of shock velocity and density of argon at very high densities, i.e., liquid density. Their apparatus, which they will describe in another publication, was designed for quite high pressures, 70,000 atmospheres.

Gases at High Temperature and Moderate Density

For moderate and low densities, the thermodynamic properties can be represented by the more traditional methods of theoretical thermochemistry, making use of the exact spectroscopic data concerning atomic and molecular energies. However, complications arising from dissociation, ionization, and excitation of higher electronic states will now require special attention.

In the usual formulation of the method of calculating thermodynamic functions, a partition function is calculated as a sum of Boltzmann factors for states of a certain elementary part of the system, such as for a molecule, with the summation supposedly extending indefinitely upward to states of

[2] See preceding chapter by Brewer and Searcy.

very high energy. However, the entire range of states is easily seen to involve an infinity of states above a region of dissociation. For some elevated temperature, the usual criterion for complete neglect of the high energy states based on the smallness of the Boltzmann factor is not fulfilled before the dissociation limit is reached, and the infinity of states immediately at hand at this energy presents a problem requiring a drastic modification. It is well known that a simple elegant solution of this difficulty exists (73, 74). According to this solution, the equilibrium between atoms and diatomic molecules is described simply as a second virial coefficient in a gas of atoms, provided that quantum effects are also included. The formation of polyatomic molecules is also solved in similar form according to the theory of cluster formation, but with necessary quantum corrections.

The quantum-mechanically exact form of the cluster theory for a mixture of a number of kinds of particles is an extension of the treatment for pure substances of Kahn & Uhlenbeck (75), Kahn (76), and Kilpatrick (77) on the one hand and the nonquantum treatment of a gas of different kinds of particles on the other. Forms of the latter given by Fuchs (78) and Muto (79) assumed additivity of pair energy between the particles of the many-component gas, as Mayer (80) had for pure gases. The required generalization includes (*a*) removal of both the additivity and nonquantum assumptions if atoms are considered as the fundamental particles, or (*b*) removal of the nonquantum assumption if nuclei and electrons are considered as the fundamental particles. The removal of the additivity hypothesis is required absolutely if the theory is to be applied to atoms as particles, for which chemical bonding is far from additive, pair wise. Added evidence that additivity is only approximate even in intermolecular interactions has been given by Jansen (81).

A direct extension of the formulas of Kahn (76) to the treatment of clusters in a gaseous mixture of many-components involves cluster integrals $b_{(l_i)}$ defined by

$$Vb_{(l_i)} \prod_i (l_i!) = \int \cdots \int U_l \prod_i^s \prod_s^{l_i} d^3r_s \qquad 24.$$

for a cluster having l_i particles of type i, with U_l as an extension of a quantity treated by Ursell (82) and later writers, to be given by

$$U_l = \sum (-1)^{k-1}(k-1)! \prod_j \frac{1}{k_j!}\left(\frac{W_j}{\prod_i (l_i)_j!}\right)^{k_j} \prod_i^s l_i! \qquad 25.$$

summed over all ways of subdividing the cluster, with k as the total number of fragments into which the cluster is subdivided, according to $k = \sum_j k_j$, k_j being the number of fragments of type j, with $(l_i)_j$ as the number of particles of type i within a single fragment of type j. W_j represents the relative probability of occurrence of an isolated fragment of type j in its particular geometric configuration as compared with its occurrence when it possesses no

energy due to interaction between its constituent particles. In nonquantum theory, W_j is a Boltzmann factor; in a quantum treatment it is a Slater sum

$$W_j = \prod_s (h^2/2\pi m_s kT)^{3/2} \sum_n \psi_n \psi_n^* \exp\,[-\epsilon_n/kT]. \qquad 26.$$

Then the cluster integrals are the equilibrium constants for cluster formation according to

$$N_{(l_i)}/V = b_{(l_i)} \prod_i (N_{(i)}/V)^{l_i} \qquad 27.$$

where V is the volume of the system and $N_{(l_i)}$ is the effective number of clusters of composition (l_i), with $N_{(i)}$ as the effective number of isolated particles of type i. It may be noted that these effective numbers of clusters or free particles are quantities giving the magnitudes of effect on properties of the system rather than giving actual numbers of "physical clusters." Hill (83) has discussed the use of physical clusters, but indicates that the simple ideal gas law for each component cluster, upon which the mass-action law of equation (27) depends, is lost when they are used. The simple result of equation (27) is not limited to the formation of molecules from smaller particles but also can include at the same time the larger grouping into clusters of molecules as given in usual gas theory. In accord with the preceding relations, the complete partition function for a mole of like clusters can be represented formally as

$$Q = \left[b_{(l_i)}\left(\frac{h^2}{2\pi \sum m_s kT}\right)^{3/2} \prod_s \left(\frac{2\pi m_s kT}{h^2}\right)^{3/2}\right]^N \left[\left(\frac{2\pi \sum m_s kT}{h^2}\right)^{3/2} V\right]^N \Big/ N! \qquad 28.$$

with the molecular free energy function for the cluster (or molecule) now defined in its usual form in terms of this Q.

A major difficulty in the theoretical application of the cluster theory to atom and atomic ion formation in gases at very high temperatures occurs as a result of the tendency toward divergence for the sum of states of high electronic excitation, even for so simple a system as a hydrogen atom or any one-electron monatomic ion. Well-known ways of avoiding this difficulty which are in use (84) were given by Fermi (85) and Urey (86) who halted the summation at the point where the orbits of electrons of different atoms would begin to "touch" each other. Planck (87) proposed a Gibbs phase integral evaluation with simplifying approximations, giving each positive ion a cell as sphere of influence. In principle, his method seems formally the most logical, as indicated by Fowler (88), except for a roughness of approximation in simplifying to a workable form.

The methods of Fermi, Urey, and Planck introduce a dependence on density which one might wish to separate from the lower energy parts of the state sums, so as to preserve the simplicity of using ideal gas functions for the separate constituents. A formulation permitting such a separation has become available by making use of a tabulation by Poirier (89) of density dependent quantities in Mayer's (90) extension of the Debye-Hückel theory of

ionic solutions to approximate the volume exclusion effects of the ions. Mayer's derivation, related to the theory of multicomponent systems of McMillan & Mayer (91), proceeds from a virial coefficient representation consistent with the general nonquantum cluster integral representation. One notes that the frequent assumption of additivity of pair energies is accurate for Coulomb forces. The effective sum of states for a cluster (atomic ion, atom, etc.) in the desired general quantum cluster representation is then so composed as to be consistent with the extension of the Ursell formula for the separation of the cluster into component fragments but with contributions involving ionic interaction limited for convenience to the interior of a sphere of constant size. For the sum of states for atoms and atomic ions, the summation may extend to levels of one electron excitation arbitrarily near the ionization limit, followed by subtraction of the classical equivalent of the part of this phase space which is outside of the chosen ionic sphere and already added by the free ion treatment of the Debye-Hückel-Mayer ion solution representation. The remaining part of a second virial approximation for the interaction of an electron with the ionic core covers the phase space region for energy running indefinitely upward from the highest level summed, with a trivial contribution for quantization of levels just below ionization also added. For the high energy region with the electron within the chosen sphere of ion size, the subtraction of the free electron part is already separately accounted for via the rigid sphere exclusion implicit in Poirier's tabulation. In following the general cluster form, the equilibrium constants for successive addition or removal of single electrons via second virial coefficients maintains a conveniently close approximation to the extended Ursell function and also to familiar chemical equilibrium equations.

The partition function for single atoms and atomic ions may thus be approximated as

$$Q^{(o)} = Q_{n_o}{}^{(o)} + q_o{}^{(o)}[Q_n{}^{(o)} + \Delta Q^{(o)} + Q_-{}^{(o)} - Q_+{}^{(o)}] \qquad 29.$$

where $Q_{n_o}{}^{(o)}$ is a sum over low lying levels ($n < n_o$) observed or of readily estimated individual energy, and $q_e{}^{(o)}$ is a weighting factor based on the Slater sum for core states with inner electrons within the ionic radius. The quantities within the bracket are one electron contributions involving: $Q_n{}^{(o)}$ as an approximate sum of states, from $n = n_o$ to $n = n_1$, using averaged observed quantum defects, $\Delta\ Q^{(o)}$ as a minute adjustment for quantization between $n = n_1$ and $n = \infty$, $Q_-{}^{(o)}$ as a phase integral contribution within the ionic radius, and $Q_+{}^{(o)}$ as a phase integral adjustment outside the atomic radius to avoid approximate duplication of coverage of phase space included in the Debye-Hückel-Mayer formulas.

Gases at moderate pressure and very high temperature can be expected to have only minor proportions of atoms combined into diatomic molecules, with still fewer triatomic and rather trivial amounts of larger molecules. The conventional quantum mechanical partition function for molecules is adequate for temperatures up to a few thousand degrees and for this region

can be refined with corrections (92) for anharmonicities, rotational-vibrational interactions, and centrifugal effects (93, 94). Its application for very high temperature becomes unsatisfactory, however, since the corrections available for these effects are then converted essentially to terms in positive powers of the temperature, giving an increasingly poorer approximation as the temperature is raised. This may become so poor that a rigid-rotator harmonic-oscillator approximation becomes preferable, though some help comes from halting the vibrational sums at dissociation (95, 96). The cluster integral treatment, on the other hand, gives good convergence at elevated temperature, with centrifugal effects directly included to an excellent approximation in the classical integral and with other effects accounted for by quantization expressed as a series approximation (97 to 100).

The Helmholtz free energy for the gaseous mixture of many constituents which reduce to one mole at standard conditions is obtainable using Mayer's formulas as

$$-\frac{A}{RT}=\frac{V}{V_o}\left\{\sum C_s\left[-\left(\frac{A^o}{RT}\right)_s-\ln C_s-\ln T/T_o\right]+\frac{2\sqrt{\pi}}{3}\frac{(\sum Z_s^2C_s)^{3/2}e^6}{(DkT)^{3/2}}\left(\frac{N_o}{V_o}\right)^{1/2}\right.$$
$$\left.+\frac{1}{2(\sum Z_s^2C_s)}\sum_{\mu\geq 0}(-1)^\mu(\sum Z_s^\mu C_s)^2\alpha^{1-\mu}f_\mu(\phi)+\frac{8\pi^3k^3T^3V_o}{45c^3h^3N_o}\right\}+\delta\left(-\frac{A}{RT}\right) \qquad 30.$$

with

a = radius of a single ionic sphere
e = electronic charge
k = Boltzmann constant
D = effective dielectric constant, ≈ 1
$\alpha = aDkT/e^2$
Z_s = ionic charge in protonic units
C_s = concentration of component s relative to that of a pure ideal gas at standard conditions
$f_\mu(\phi) = b_\mu(\phi)+g_\mu(\phi)$, obtainable from functions tabulated by Poirier (89). (μ is a running index.)

$$\phi=\frac{2\alpha(\pi\sum Z_s^2C_s)^{1/2}e^3}{(DkT)^{3/2}}\left(\frac{N_o}{V_o}\right)^{1/2}.$$

The quantity

$$\delta\left(-\frac{A}{RT}\right)$$

given by

$$\delta\left(-\frac{A}{RT}\right)=-\frac{V}{V_o}\left[\frac{(B_{eff}-B_m)}{V_o}(\sum C_s)^2+\frac{(C_{eff}-C_m)(\sum C_s)^3}{2V_o^2}\right.$$
$$\left.+\frac{(D_{eff}-D_m)(\sum C_s)^4}{3V_o^3}\cdots\right] \qquad 31.$$

is a correction for such changes as may be required to convert from the calculated equation of state (represented by equivalent virials B_m, C_m, $D_m\cdots$, as given by cluster theory, using a single rigid ionic sphere of exclusion in Poirier's tabulation for Mayer's theory) to the actual equation

of state as represented by actual effective virials (B_{eff}, C_{eff}, $D_{eff} \cdots$) for the mixture if such a better approximation is at hand.

The chemical equilibrium between various constituents then follows for a reaction producing ν_s moles of the general constituent Y_s, expressed as: $\sum \nu_s Y_s = 0$, (ν_s positive for products) as

$$\prod_s C_s^{\nu_s} = (T_0/T)^{\Sigma\nu_s} \exp\left[\sum \nu_s\left(-\frac{F^\circ - H_0^\circ}{RT}\right), -\frac{\Delta H_0^\circ}{RT}\right]\gamma_1\gamma_2\gamma_3 \qquad 32.$$

where

$$\gamma_1 = \exp\frac{\sqrt{\pi}(\sum Z_s^2 C_s)^{1/2}(\sum \nu_s Z_s^2)e^3 N_0^{1/2}}{V_0^{1/2}(DkT)^{3/2}}, \qquad 33.$$

from the simple Debye-Hückel theory, and

$$\gamma_2 = \exp\left\{(\sum Z_s^2 C_s)^{-3}\sum_{\mu \geqq 0}(-1)^\mu \alpha^{1-\mu}[(\sum Z_s^2 C_s)(\sum Z_s^\mu C_s)(\sum \nu_s Z_s^\mu) f_\mu(\phi) - (\sum Z_s^\mu C_s)^2(\sum \nu_s Z_s^2) g_\mu(\phi)]\right\}, \qquad 34.$$

based on Mayer's extension to the ion solution theory. The quantity γ_3 is given by

$$\gamma_3 = \exp\{-\sum \nu_s(\partial/\partial C_s)[(B_{eff} - B_m)(\sum C_s)^2/V_0 + (C_{eff} - C_m)(\sum C_s)^3/2V_0^2 + (D_{eff} - D_m)(\sum C_s)^4/3V_0^3]\} \qquad 35.$$

including further the dependence of B's, C's, D's, etc., on the C_s's corresponding to the usual deviations of gases from ideality.

It appears appropriate to emphasize that thermodynamic functions obtained using the cluster treatment are not significantly different from those obtained with the more familiar methods of calculation, except at rather high temperatures. The differences are extremely minute at ordinary temperature and usually negligible even up to temperatures of a few thousand degrees.

An advantage of the cluster method is that the functions obtained are suited to the law of mass action in its simplest form. Of course, if the density is so high that high order clusters should be considered or if the temperature is also so high that ion solution theory is required, then a modification of the simple equilibria is called for as indicated by γ_1, γ_2, and γ_3 of equations (33–35) in accord with the well-known principles of chemical equilibrium in their general formulation concerning activity coefficients.

The solution of the equations for equilibrium together with the equations for conservation of electric charge and atomic nuclei may conveniently be made using digital computers. At very high temperature such that diatomic and larger molecules are entirely negligible in amount, the problem is simplified very markedly by their omission. At intermediate temperatures where the number of constituents is large, the entire calculation is somewhat complex.

One of the early applications of the chemical equilibrium method to mixtures of atomic ions was in the determination of temperature and pressure in stellar atmospheres. The theory of Saha (101) with refinements by Fowler & Milne (102) thus gave the interpretation of the spectral sequence of the various star types. Calculations for air at elevated temperatures have been made by Bethe & Teller (103), Bethe (104), Fuchs *et al.* (105), Brinkley *et al.* (106), Hirschfelder & Magee (107), Hirschfelder & Curtiss (108), Krieger & White (109), Davies (110), Hilsenrath & Beckett (111), and Gilmore (43). Recent extrapolations of functions for constituents of air to elevated temperatures include tables of Fickett & Cowan (113) to 12,000°K. and Gilmore, to 24,000°K.

Gilmore (43) has given a comparison between Latter's (45) calculations on the equation of state of air by the FMT method and his own calculations and those of Fuchs *et al.* (105) by chemical equilibrium methods which take shell structure explicitly into account. The comparison indicates that the pressure and energy isochores according to the FMT and chemical methods have a very similar trend. The FMT isochores, however, are smooth while the presumably more correct chemical isochores exhibit inflection points at the temperatures at which the different shells are ionized. These inflections are accentuated in such properties as specific heat which depend on derivatives of energy.

The Thomas-Fermi and the cluster treatments are suitable approximations in different temperature-density regions. The former gives an approximate quantum statistical representation of the energy states of the system at high densities. It appears to be much more accurate at high than at low temperatures. The latter employs more accurate energy states, obtained in part from spectroscopic observations, in a series development appropriate to gases at low densities. As densities are increased series convergence decreases and requirements for data increase; lack of information on the higher energy states of molecules, on the density dependence for the states, and on the forces between molecules in excited states presents many difficult experimental and theoretical problems which have scarcely been considered as yet.

At virtually any temperature, the equation of state and related thermodynamic properties can be evaluated with fairly high accuracy at either quite low or quite high densities, but not in an intermediate region beyond the laboratory experimental range yet with an interesting occurrence in the core of the earth.

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THE SOLID STATE[1]

By F. J. Blatt[2,3] and C. T. Tomizuka[2,4]
Department of Physics, University of Illinois, Urbana, Illinois
and
L. M. Slifkin
Department of Physics, University of North Carolina, Chapel Hill, N. C.

In writing this review, space limitations faced the authors with a choice between presenting an annotated bibliography covering a large area of solid state research on the one hand, or writing a review article in which only a rather small segment of the field would be discussed in a somewhat more detailed and systematic manner. We have decided to adopt the latter procedure.

The selection of topics was based in large measure on a desire to review the fields in which substantial progress has been made in recent years so that these pages might serve the purpose of synthesizing a large body of experimental and theoretical knowledge. In part, the topics presented also reflect the interests of the authors.

POINT IMPERFECTION IN METALS

Vacancies and Interstitials

Numerous approaches have been made in the past few years to investigate the nature of vacancies and interstitials in metals. These approaches can generally be classified into two major categories: 1. that which makes use of imperfections present in metals in thermal equilibrium, and 2. that which employs some method of introducing excess imperfections.

Volume diffusion.—The typical example of the first approach is the measurement of volume diffusion in pure metals. A review article by Kleppa (1) and an article by Lazarus (2) give sufficient background in the recent development in this field. The activation energy E_D of a diffusion process gives the sum of the energy E_f required to form an imperfection and the energy E_m which is the activation energy for the motion of a diffusing atom into an adjacent imperfection. Some experiments have been proposed to identify the nature of the imperfections (3, 4, 5) i.e., to see whether vacancies or

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[3] Present address: Department of Physics, Michigan State University, East Lansing, Michigan.

[4] Present address: Institute for the Study of Metals, University of Chicago, Chicago, Illinois.

interstitials are in operation. These proposals either invited serious theoretical objections (6, 7, 8) or implied experimental difficulties.

Consistent attempts are being made by Shirn, Wajda & Huntington to determine the mechanism of diffusion in noncubic metals such as zinc (9), thallium (10), and cadmium (11) by making use of the dependence on the mechanism of diffusion of the ratio of diffusion coefficient along the c-axis to that along the basal plane. Their results on cadmium are not as clear-cut as those on zinc or thallium, which indicate a vacancy mechanism. Similar analysis is made by Nicholas (12) on tin using the data of Fensham (13, 14). No definite conclusions are drawn as to the mechanism in operation.

In addition to the standard tracer technique of measuring self-diffusion, the nuclear resonance technique involving the measurement of the spin-lattice relaxation time, T_1, and of the inverse line width (spin-spin relaxation time), T_2, has been developed recently. This method makes use of the fact that a translational diffusion in a lattice gives rise to a fluctuating local magnetic field which interacts with the nuclei thereby causing changes in T_1 and T_2. This method offers the means of measuring self-diffusion where no suitable radioactive tracers are available. Holcomb & Norberg (15) measured the nuclear spin resonance in lithium, sodium and rubidium. Employing the lattice diffusion theory of Torrey (16), they obtained the activation energies of self-diffusion in these metals. Their results on lithium and rubidium are consistent with the thermodynamical relation of Nachtrieb *et al.* (17) and the activation energy for sodium self-diffusion is in good agreement with tracer results of Nachtrieb, Catalano & Weil (18).

Measurements of internal friction as a function of temperature offer an alternative method for measuring diffusion in certain alloys [Zener (19), Snoek (20)]. Here again the reader is referred to the review by Kleppa (1) and the one by Nowick (21).

The fact that the measurement of volume diffusion cannot by itself give concrete information on the individual values of E_f and E_m directly, leaves room for theoretical considerations such as those by Buffington & Cohen (22). Assuming the vacancy mechanism, they proposed a procedure for estimating the fraction of the activation energy for self-diffusion that goes into the elastic straining of the lattice during the motion of a diffusing atom. For b.c.c. and f.c.c. lattices, this ratio appears to be consistently larger than one half.

Specific heat and resistivity.—In order to perform a direct measurement of E_f and E_m separately, it is necessary to depart from the conventional measurement of the activation energy of volume diffusion, though one can still remain within the scope of the first approach, which employs only the imperfections in thermal equilibrium. Some years ago Carpenter (23) measured the specific heat of sodium, lithium and potassium and observed an anomalous rise setting in at about 100 degrees below the melting point, the anomaly increasing as the temperature approached the melting point. This excess specific heat was attributed to the formation of vacancies, and a for-

mation energy of about 0.25 ev for potassium and sodium was obtained (24). This value implies that the concentration of defects is of the order of 0.1 per cent at the melting point. Similarly, the value of 0.27 ev for rubidium was determined by Preston-Thomas (25).

MacDonald (26) measured the electrical resistivity of lithium, sodium and potassium over a wide range of temperature and observed an anomalous rise of resistance starting at about 80 degrees below the melting point. Assuming that this increase is due to vacancies in thermal equilibrium, it is possible to arrive at an independent estimate of the activation energy for formation of vacancies. Values in the neighborhood of 0.4 ev are obtained for these metals. Using Jongenburger's calculation (27) on the scattering cross section, the above value corresponds to approximately 0.1 per cent vacancy concentration at the melting point. Similar measurements on rubidium yielded a formation energy of approximately 0.6 ev, which is considerbly larger than the value obtained from specific heat measurement [MacDonald (28)]. The discrepancy has been attributed to defects of small formation energy, which make large contributions to the specific heat, but which have a small cross section for electron scattering. This duality in the interpretation renders the results on sodium somewhat questionable. Meechan & Eggleston (29) measured the electrical resistance of copper and gold as a function of temperature. A dependence $\rho = A_0 + A_1 T + A_2 T^2$ of the resistivity on temperature was assumed to be the normal behavior. The deviation from this form at higher temperatures was attributed to the presence of vacancies and the activation energy for the formation of vacancies was estimated. In view of the fact that the addition of a cubic term to the temperature dependence eliminates the deviation, their analysis is subject to some question.

The experiments described above give the energy to form a vacancy directly but they do not directly yield the energy for the motion of vacancies. The latter is estimated from the former only through the knowledge of the activation energy for diffusion. In order to obtain an experimental value of E_m, it is generally necessary to introduce an excess number of imperfections in the lattice by one of the following procedures: (*a*) quenching in of thermal imperfections from high temperatures, (*b*) damaging of the solid by high-energy particles, (*c*) a nuclear resonance technique which does not make use of the artificial introduction of excess imperfections.

Quenching-in of thermal vacancies.—Kauffman & Koehler (30) measured the increase in electrical resistance produced by rapid quenching of a specimen of pure gold wire from various temperatures into a liquid nitrogen bath. Assuming that the anomalous increase in resistance is due to the quenching-in of thermal imperfections, the value of $E_o = 1.28$ ev was obtained. Under the same assumption, E_m was determined by the isothermal annealing of the quenched specimen and was found to be 0.68 ev, which is in good agreement with results of Overhauser (31) on radiation-damaged copper. Thus the activation energy for self-diffusion can be deduced as $E_4 = E_f + E_m = 1.96$ ev, which agrees with the existing data on self-diffusion but shows consider-

able deviation from the more recent value of 1.71 ev obtained by Okkerse (32). The fact that Kauffman & Koehler's annealing curve suggests second order kinetics places some ambiguity in the meaning of their value of E_m since it is not necessarily identical with the energy of motion of a single vacancy.

Actually the method of freezing-in of imperfections was first demonstrated by Nowick & Sladek (33) and by Roswell & Nowick (34) for a silver-zinc substitutional solid solution. They employed anelastic measurements to obtain the value of 0.84 ev for E_m and 0.5 ev for E_f for vacancies at a 30 per cent zinc composition. It should be noted that the ratio of the energy of formation to the total activation energy of diffusion is considerably smaller in this instance than the results of the other investigators but is in agreement with the theory of Buffington & Cohen (22). However, the smaller value of this ratio could be attributed to a possibly smaller energy to form a vacancy in the alloy, whereas E_m is probably not appreciably affected. Despite its limitations, anelastic measurements have an advantage over the other types of experiment in that the imperfections contributing to anelasticity can be identified as those contributing to diffusion.

Radiation damage.—The annealing process of metals by bombardment with high energy particles has been studied intensively in recent years. Even though this field was initially started as the material problem for the construction of nuclear reactors, it led to a more fundamental study of defects in solids, because of the exceedingly large fraction of excess imperfections introduced. Solids are irradiated either with neutrons or with charged particles, such as deutrons and electrons; and various physical properties are measured directly after the irradiation and during the process of annealing. Recent reviews of this subject are given by Broom (35), Koehler & Seitz (36), and Glen (37).

Volume expansion has been reported by McDonnell & Kierstead (38) on deuteron-irradiated copper. This expansion presumably is due to the production of vacancies and interstitial atoms by irradiation. The initial rate of expansion is about 1/10 of the rate predicted by Seitz (39).

In order to prevent previously observed annealing during irradiation at liquid nitrogen temperature (31), Cooper *et al.* (40) subjected copper, silver and gold to deuteron irradiation near 10°K. and measured resistivity changes. It was found that a unique annealing process took place at about 40°K. for copper and 30°K. for silver. This was attributed either to the motion of interstitial atoms or to recombination of interstitial-vacancy pairs. The estimated activation energy for the process is about 0.1 ev which is the value calculated by Huntington (41) for the motion of interstitials. It would be reasonable to assume that this motion of interstitials actually takes place during this stage of annealing. The second unique annealing stage was observed at about −30°C. and was interpreted in terms of the motion of lattice vacancies with an activation energy of 0.68 ev, in agreement with Overhauser's results (31). The bimolecular nature of the process

at −30°C. has been explained in terms of the formation of mobile divacancies [(30), Blatt (42)]. On the other hand, analogous results of neutron irradiation on copper by McReynolds *et al.*, (43) were interpreted by them as the bimolecular combination of interstitial atoms and vacancies with an activation energy of 0.6 ev. These conflicting views and a few more [e.g. Brinkman, Dixon & Meechan (44)] are yet to be resolved.

Notable efforts have been made recently to assess theoretically the energy required to displace an atom into an interstitial position [Huntington (45)], the average number of interstitial-vacancy pairs to be expected per primary displaced atom due to monoenergetic radiation [Seitz (39), Seitz & Harrison (46), Snyder & Neufeld (47, 48)], and the contribution of point defects to electrical resistivity [Dexter (49), Jongenburger (27), Blatt (42)].

Nuclear magnetic resonance method.—A new method of determining E_f and E_m separately by a nuclear magnetic resonance technique was proposed by Bloembergen (50), and by Holcomb & Norberg (15). The time dependent quadrupole effect in a crystal with an appreciable vacancy concentration makes a contribution to $1/T_1$ proportional to $\exp((-E_f+E_m)/kT)$. Thus relaxation by quadrupole coupling contains a different combination of energies than the dipolar interaction associated with diffusion. If this quadruple term predominates at high temperatures, one has the means of determing these two energies separately. This happens usually only at temperatures close to the melting point. There is as yet no clear-cut experimental evidence of this effect.

Resistivity Minimum

The discovery (51) of the minimum in the electrical resistivity of gold wire in the liquid helium temperature range was followed by many other examples of resistivity minima. It is now known that only a small amount of impurity is necessary to produce this effect and, except in the recent report of Pearson (52), these minima were observed only in polycrystalline wires. Consequently, there have been investigations to clarify the role of grain boundaries in this effect as well as to establish the type of impurities which give rise to a resistance miniumum. An extensive study has been carried out by MacDonald & Pearson (53, 54) on dilute alloys of copper, who reported anomalies in thermoelectric power as well as in resistivity.

Blewitt *et al.* (55) cold worked high purity single crystal wire of copper and found that the resistance minimum appeared after the wire was annealed and recrystallized. An explanation of this grain boundary effect was given by Koehler (56) in terms of Pauli principle scattering which becomes predominant as the temperature in lowered. On the basis of a critical experiment, Cohen & Barrett (57), however, expressed the view that some imperfections other than grain boundaries were present in the recrystallized specimens of Blewitt *et al.* Experiments by Schmitt & Fiske (58) also indicated that scattering by grain boundaries itself contributes very little to the resistance minimum. Bhatia (59) proposed a theory similar to the Bardeen-Froehlich

theory of superconductivity but with a weaker interaction to explain the resistance minimum and thermoelectric anomaly.

In order to clarify the essential features of the resistivity minimum, it is evident that more experimental data are needed; especially the study of the effect of grain size should reveal the role of grain boundaries except that, as pointed out by Cohen & Barrett (57), it is impossible to distinguish between a pure grain boundary effect and effects of segregation of impurities at the boundaries.

PROPERTIES OF GERMANIUM AND SILICON

Dislocations in Germanium and Silicon

The concept of lattice dislocations has been extensively employed in the interpretation of the properties of metal crystals (60) and has been found useful in understanding many phenomena exhibited by ionic crystals (61). Until 1952, however, the properties of these imperfections in germanium and silicon were unknown.

Germanium and silicon differ from metals in many respects other than their electrical properties. For example, they are not ductile at room temperature and readily shatter brittlely. Much of the difference may be traced to the fact that, whereas the atoms in metals are held together by non-directional unsaturated bonds, germanium and silicon crystallize in the diamond lattice, each atom partipating in four covalent bonds strongly oriented along tetrahedral directions.

Lack of plasticity in germanium and silicon may be due to immobility of dislocations or their absence. That dislocations are present was demonstrated by the observation that a properly etched germanium surface often exhibits a line of small pits located along a small-angle boundary (62). Now, the extra half-plane of an edge dislocation acts as a wedge, and if one arrays parallel dislocations with vertical half planes such that the edges of the "wedges" are one above the other, a small-angle boundary results. Vogel *et al.* found that the measured disorientation across the boundary invariably agreed with that calculated assuming each etch pit to be the intersection of an edge dislocation with the crystal surface.

Just prior to this work, it was found by Gallagher (63) that single crystals of germanium and silicon would deform plastically above about 500°C. and 900°C. respectively. After flow, slip lines appeared, and the specimens had retained their single-crystallinity. This morphology is characteristic of deformation of metal crystals and suggests that here deformation also proceeds by slip [the slip planes in Ge are {111}]. It follows that, in contrast to metals, dislocations in germanium and silicon can glide only at elevated temperatures. Two other new features also were found: (*a*) In the lower temperature range (500°C. to 600°C. for germanium) plastic flow did not commence immediately upon application of stress; instead there was an induction period which decreased with increasing temperature and was of the

order of minutes at 500°C. (*b*) In germanium and silicon the influence of plastic flow on conductivity was much more pronounced than in metals.

Gallagher's results have been discussed by Seitz (64). He proposed that an edge dislocation in germanium involved two adjacent [110] half-planes and interpreted the incubation period in terms of anchoring of dislocations to solute atoms, as discussed for the case of metals by Cottrell (65, 66). An atom of germanium at an edge dislocation will have one free valence bond and might be expected to interact strongly with appropriate foreign atoms, strongly pinning the dislocation. At elevated temperatures, thermal fluctuations enable the stress to pull the dislocations free of their anchors, and the incubation period is determined by the time required for this process. Seitz proposed that the incubation time should be expressible as a constant τ_0 times a factor exp(Q/RT), and estimated τ_0 on the basis of the solute-dislocation complex and also of diffusion of solute atoms. Further measurements of Gallagher (67) established the validity of the proposed relation but gave values of τ_0 1000 times larger than calculated. It may be that the matter is more complicated, involving dislocation-dislocation interactions.

Further evidence for the soundness of the above model was provided by Baker *et al.* (68), who found that between 500°C. and 600°C. the stress required to produce plastic flow at a frequency of 37 kc/sec decreased with time under stress, the decrease being more rapid at higher temperatures and greater amplitudes of the ultrasonic stress.

To explain the electrical effects of plastic flow Shockley (69) proposed that the free valence bond at a dislocation act as an acceptor, giving a qualitative account of the observation (63) that plastic flow decreases the electron concentration of *n*-type specimens and may even convert an *n* to a *p*-type specimen (70). Landauer (71) took into account the effect of segregation of electrically active impurities at dislocations on the carrier density. Mayburg (72) showed this to be important by studying the resistivity of silicon crystals quenched from high temperatures. His results can be understood if acceptors collect at dislocations below about 900°C. and thus lose their acceptor property; above 900°C. the impurities "evaporate" from the dislocations. It is interesting that the critical temperature of 900°C. is just that at which silicon becomes plastic, presumably because at this temperature the dislocations can escape from their impurity atmospheres. There are, however, related experiments which do not conform with this picture (73).

Landauer also considered the effect of the local stress field about a dislocation, which should give rise to trapping and recombination centers, in agreement with the observation (74, 75, 76) that minority carrier lifetimes are very small in deformed cystals. These local dilatations also appear to decrease the forbidden energy gap (77).

Pearson, Read & Morin (74, 78, 79) suggested that a dislocation in *n*-type material would become negatively charged by virtue of occupied acceptor states. This line charge would then be surrounded by an extensive cylindrical region of positive space charge, thereby reducing the mobility of

electrons both by scattering and by the bending of the electron flow lines.

Pearson *et al.* (74) bent n and p- type germanium crystals at 650°C. and studied etch patterns, conductivity, Hall effect and minority carrier lifetimes. The etch pits were found to be arrayed along lines in the slip plane orientation, as would be expected of dislocations, and their observed density was about one-third the calculated minimum dislocation density (10^7/cm.^{2}) necessary to produce the deformation. Since the pits were very closely spaced, this discrepancy could be accounted for by inadequate resolution in the counting. Conductivity and Hall effect data showed that deformation had greatly decreased both the number and mobility of majority carriers of the n-type specimen but had produced only a negligible effect on these quantities for the p-type specimen, consistent with the interpretation of the dislocation as an acceptor. Analysis of the data indicated an acceptor level about 0.2 ev below the conduction band.

Tweet (80) has shown that plastic deformation of germanium also introduces acceptor states at about 0.1 ev above the valence band. These annealed out in about one hour at 800°C. and were attributed by Tweet to vacanices formed during deformation (61, 81).

Band Structure of Germanium and Silicon

The basic concepts of the band theory of crystals were described in an earlier volume of this series (82). In the last three years several experimental and theoretical advances have been made which permit a detailed description of the band structure of silicon and germanium. This new knowledge has enabled us to interpret and unify the results of a wide variety of experiments. A suggestion of the beginning of this development may be found in the paper of Bube *et al.* (83). The extensive progress that has taken place since then is outlined here.

Effective mass.—The energy of a free electron is given by $E=\hbar^2k^2/2m$, where k is the magnitude of the wave vector and m the electron mass. In a crystal, however, an electron moves in a potential which is periodic in the lattice. The energy may now be a complicated function of $\mathbf{k}$, with extrema not necessarily at the origin of $\mathbf{k}$-space. If we expand the energy in a power series about one of the extrema the leading term, apart from an additive constant will be quadratic in the components of $\mathbf{k}$. Neglecting higher order terms we now define the effective mass tensor by $m_{ij}^*=\hbar^2[\partial^2E/\partial k_i\partial k_j]^{-1}$. The effective mass is thus a direct measure of the shape of the energy band in the vicinity of the extremum. It can be shown that electric and magnetic fields act upon the electron in the crystal as though it were free but of mass m^* (82, 84).

Early inferences concerning band structure.—Until recently electronic properties of germanium and silicon were interpreted in terms of the simple assumption that the valence band has its maximum energy and the conduction band its minimum energy at the origin of $\mathbf{k}$-space. Cubic symmetry then required that near the extrema the surfaces of constant energy be spheres.

Experimental results were fitted to theoretical predictions by employing m^* as an adjustable parameter. Unfortunately, fit of data to theory is often not very sensitive to m^*; moreover, different types of experiments often gave contradictory values for m^*. The rather unsatisfactory state of affairs which existed is summarized in the next three paragraphs.

Extensive measurements of mobilities of electrons and holes in germanium and silicon by Prince (85, 86), Morin (87), Debye & Conwell (88), and Morin & Maita (89) indicated that for electrons m^* is about $m/4$. The data for holes were difficult to interpret because the mobility did not exhibit the theoretical temperature dependence, and it was proposed that the valence band energy maximum was not at $\mathbf{k}=0$. The ratio of Hall to drift mobility for holes was found to increase anomalously with temperature to a value close to 2 at room temperature. An explanation in terms of multiple energy surfaces in the valence band was suggested.

Measurements of magnetic susceptibility of germanium by Stevens & Crawford (90) gave $m^*/m=1/4$ for holes and 1/6 for electrons. From measurements of dielectric constant at microwave frequencies Benedict & Shockley (91, 92), Goldey & Brown (93), and D'Altroy & Fan (94) obtained the following range of values for m^*/m: 0.09−0.6 (electrons) and 0.3−0.6 (holes).

The magnetoresistance of germanium of controlled purity was measured by Estermann & Foner (95) using polycrystalline material. Pearson & Suhl (96) employed single crystals and studied in detail the anisotropy of the magnetoresistance. For n-type germanium a large longitudinal magnetoresistance was found which was incompatible with the assumption of spherical energy surfaces. For p-type this longitudinal effect was very small but the transverse effect was anomalously large, leading Shockley (97) to suggest that the valence band was triply degenerate.

Band structure calculations and cyclotron resonance experiments.—The experiments just described showed that the simple model for the band structure was inadequate, but they did not, of themselves, give the details of the correct picture. What was needed was a reliable independent calculation of the band structure or some direct experimental means of studying it. Fortunately, both appeared.

Herman (98) has made a detailed theoretical study of the band structure of the diamond lattice, with emphasis on germanium. The effect of spin-orbit coupling on the bands has been discussed by Elliott (99). The work has been extended to silicon by Woodruff (100). These investigations indicated that for both germanium and silicon the valence band actually consists of three doubly degenerate bands each with its maximum energy at $\mathbf{k}=0$. Two of these bands are degenerate at $\mathbf{k}=0$ but have different effective masses. The third band lies well below the other two and hence would not ordinarily be occupied by holes. For the conduction band, it was shown to be quite probable that the energy minimum is not at the origin, but that there are either eight equivalent minima along the [111] axes or six minima along

the [100] axes in **k**-space. In any event, the energy is not isotropic in **k**-space near the energy minima; rather, the constant energy surfaces in the conduction band are concentric prolate spheroids, with major axes along the radius vector from the origin to the minimum.

Cyclotron resonance experiments (101, 102, 103) in germanium and silicon by Dresselhaus *et al.* (104) and Lax *et al.* (105) confirmed these results. In the presence of a magnetic field an electron (or hole) will move in an orbit with angular frequency eH/m^*c. If an alternating electric field of the same frequency as that of the orbital motion is applied in the plane of the orbit, energy is absorbed by the carriers. In order that a resonance peak be observed the carriers must complete on the average a full orbit before suffering a collision. To achieve this condition the experiments are carried out at microwave frequencies, liquid helium temperatures, and with high purity specimens. Free carriers may be produced by optical excitation. The results show that for germanium the conduction band minima are along the [111] axes, and the constant energy surfaces are prolate spheroids with effective masses of 1.58 m (along [111]) and 0.082 m (normal to [111]). For silicon the conduction band minima are along [100]; the corresponding effect masses are 0.97 m (along [100]) and 0.19 m (normal to [100]). The valence bands are as predicted by Herman. For the two bands of maximum energy at $\mathbf{k}=0$ one is nearly isotropic with $m^*/m=0.042$ for germanium and 0.16 for silicon. The other band in each substance is somewhat anisotropic, the energy surfaces resembling warped spheres; the average effective mass for this band is about 0.3 m for germanium and 0.5 m for silicon.

Implications of the band model.—A discussion of the transport properties in the new model is presented in a later section. Here we consider a number of other phenomena with emphasis on their interpretation in terms of the band structure.

The piezoresistivity of germanium and silicon was studied by Smith (106). Small effects are to be expected from changes in mobility of the carriers due to effects of elastic strain on thermal vibrations, and from changes in carrier density due to a dependence of the energy gap on strain. For several orientations, however, a very large value for the piezoresistance coefficient was found. Herring (107) has suggested the following explanation for n-type germanium and silicon: The anisotropy of the effective masses leads to an anisotropic conductivity for each conduction band minimum, or "valley." Because the several valleys are symmetrically located in **k**-space and are ordinarily equally populated the crystal as a whole shows isotropic conductivity. If an appropriate stress is applied, however, the energy minima of some valleys may be raised and others lowered, causing some valleys to have greater electron populations than others; the electrical conductivity will now be anisotropic and greatly changed in certain directions. In addition to this effect, the probability of scattering of electrons from one valley to another will be changed. Herring's theory predicts that these "anomalously" large piezoresistance coefficients should vary as $1/T$; this has been confirmed

experimentally by Keyes (108). The results for *p*-type specimens have been interpreted by Adams (109) in terms of the effect of the elastic strains on the multiple energy surfaces of the valence band.

Because the energy minima in the conduction band are not at $\mathbf{k}=0$ a difficulty arises in comparing the values for the energy gap obtained thermally with that obtained optically. One can show that optical excitation of an electron from the valence to the conduction band must leave the electron's wave vector essentially unaltered. Since the minimum energy in the conduction band and the maximum energy of the valence band occur at different $\mathbf{k}$ values, the "optical" gap should be larger than the thermal by just the difference between the conduction band energy at $\mathbf{k}=0$ and the minimum energy in that band. Experimentally, however, thermal and optical gaps agree. This problem was discussed by Hall, Bardeen and Blatt (110) who showed that "indirect" transitions are quite probable; these involve emission or absorption of lattice vibrational quanta thus conserving the total wave vector. Support for this interpretation comes from measurements of absorption coefficients by Dash & Newman (111) and MacFarlane & Roberts (112). Radiation emitted from recombination of holes and electrons has been observed by Haynes & Briggs (113), Newman (114), and Haynes (115). Two peaks have been found, presumably corresponding to indirect and direct transitions. Emission and absorption results are in good agreement.

The energy gap in alloys of germanium and silicon has been studied by Johnson & Christian (116), who found that the optical absorption edge increases monotonically with increasing proportion of silicon. Their results show that the gap may be represented as a function of composition by two straight lines meeting at about 14 per cent silicon. Herman (117) has suggested an explanation of these results in terms of changes of the band structure with alloying. Magnetoresistance measurements by Glicksman (118) and conductivity measurements by Levitas, *et al.* (119) and Levitas (120) are in essential agreement with Herman's interpretation and the results of Johnson & Christian, though the conductivity results appear to differ in some details.

Absorption coefficients of germanium and silicon in the infrared region of wavelengths beyond the band-to-band edge were studied by Fan & Becker (121), Kaiser, *et al.* (122) and Briggs & Fletcher (123). Two anomalies were observed: (*a*) the absorption attributable to free carriers was much in excess of that predicted by the Drude-Zener theory; (*b*) three distinct absorption bands were observed for *p*-type germanium. These results have been explained by Kahn (124). The large absorption by free carriers was shown to be consistent with the small effective masses given by cyclotron resonance experiments. The fine structure in *p*-type germanium was interpreted in terms of optically induced transitions of holes from one energy band to another within the valence band complex. Similar structure was predicted for *p*-type silicon at wavelengths longer than have been employed to date.

An unresolved question is whether the conduction band minima lie at the surface of the Brillouin zone or in its interior; if, as theory suggests, the former is the case, there should only be four minima since opposite points on the Brillouin zone are equivalent. Susceptibility measurements of Stevens *et al.* (125) and of Enz (126) are consistent only with the assumption of four minima, and a careful examination of Hall data also points to this conclusion (127).

Transport Properties

The many-valley model.—We have seen that all available information on germanium and silicon indicates that the structure of the valence and conduction bands of these materials is not of the simple form; that is, they do not have non-degenerate spherical energy surfaces in $\mathbf{k}$-space with extrema at $\mathbf{k}=0$. It is thus not adequate to described the transport phenomena in these substances in terms of elementary theories which presuppose the existence of spherical energy surfaces (128). As a matter of fact, as has already been pointed out, the first indications of a complex band structure were observed anisotropies in the magnetoresistance.

Meiboom & Abeles (129, 130), and concurrently Shibuya (131, 132, 133), calculated the conductivity tensor in the presence of a magnetic field assuming energy surfaces of the type described in the preceding section. These workers were able to show that the assumed conduction band structure could explain the experimental observations. More recently Herring (107) has extended the transport theory to the "many valley" model, appropriate to n-type germanium and silicon. Herring derived expressions for drift mobility and its temperature dependence, thermoelectric power, Hall effect and magnetoresistance, and piezoresistance.

A particularly interesting feature of the many valley case is that two distinct types of scattering processes can occur and must be considered in detail. One, intravalley scattering, is analogous to that which also limits the mobility in the simple case, and in the lattice scattering range involves only low energy, long wavelength phonons. In addition to these processes an electron in a certain state on a given energy ellipsoid may be scattered to a state on an energy ellipsoid located along a different symmetry axis. This intervalley scattering requires the interaction of electrons with phonons of wave vector comparable to a reciprocal lattice vector, and, hence, is not significant at temperatures less than about $\Theta/10$, where Θ is the Debye temperature. One consequence of intervalley scattering is that the temperature dependence of the mobility may differ, in a limited temperature range, from the $T^{-3/2}$ law predicted by the simple model. Corresponding deviations are to be expected in the same temperature range for piezoresistance, thermoelectric power and other transport effects.

Previous calculations based on the simple model have recently been extended to the many valley case. At very high fields, electrons in semicon-

ductors may, within a mean free path, gain so much energy from the field that the electron distribution is no longer in thermal equilibrium with the lattice. When this occurs the mobility exhibits a field dependence (134, 135). In other words, Ohm's law is no longer satisfied. This so-called "hot electron" problem had been discussed by Shockley (136) and Yamashita & Watanabe (137) in terms of the simple model; this theory, although giving a satisfactory qualitative account of the phenomenon, predicted a critical field for onset of the effect which disagreed with experiment by a factor of about three. Shibuya (138) has recently applied the many valley model to this problem; he was able to obtain somewhat better agreement with experiment although a significant discrepancy remains which might well be removed by consideration of intervalley scattering which was not taken into account by Shibuya.

The mobility of carriers in thin films, such as occur in an inversion layer at the surface of a semiconductor, was discussed by Schrieffer (139) using the simple model. The analysis was extended to the many valley model by Ham & Mattis (140) who found that the mobility in the film should be very sensitive to the orientation of the normal of the film surface relative to the crystallographic directions.

All of the calculations of the transport properties, even for the many valley case, have assumed that the collision integral in the Boltzmann equation could be described in terms of a relaxation time which may depend on electron energy but is isotropic in $\mathbf{k}$-space. While this is probably a fair approximation for lattice scattering (107), recent work of Ham (141) shows that the relaxation time for impurity scattering is highly anisotropic. Suitable detailed calculations of transport properties using anisotropic relaxation times have not yet been published.

The transport properties of p-type silicon and germanium have been treated in some detail by Willardson, Harman & Beer (142, 143). These workers assumed that the valence band structure could be represented adequately by two simple bands of different curvature but degenerate at $\mathbf{k}=0$; they then derived expressions for mobility, Hall effect, and transverse magnetoresistance which give very good agreement with experimental results. One outstanding property of p-type silicon and germanium, namely the unusual temperature dependence of the mobility in the lattice scattering range, does not find an explanation in the model of Willardson *et al.* Theoretically, the mobility should depend on $T^{-3/2}$. This relationship is, in fact, very nearly valid for n-type germanium. However, in p-type samples and n and p-type silicon the mobility goes as about $T^{-2.3}$ (85, 86, 87). At the time of writing no satisfactory explanation of this discrepancy between theory and experiment has been advanced, and the problem remains one of the most interesting and important in the field of semiconductor research.

Since the valence band consists of two degenerate bands with different effective masses one should, in a Haynes & Shockley (144) drift experiment,

observe two pulses for p-type specimens, one for each type of hole. An unsuccessful attempt to observe these two pulses has been made by Harrick (145).

Thermoelectric power.—Frederikse (146) discovered some years ago that the thermoelectric power of germanium shows an anomalous increase at low temperatures which could not be explained by the current theories of thermoelectric power (147, 148, 149). He showed that Makinson's analysis (150) of the influence of a non-equilibrium phonon distribution on electron transport could explain the experimental results. These ideas have since received considerable attention (151, 152, 153) and we shall here indicate briefly the cause for the additional thermoelectric effect. If a thermal gradient is maintained in any material this gradient will give rise to a flow of energy from the hot to the cold end of the sample. In a metal or semiconductor part of this energy is carried by the electrons; a portion, however, is also carried by lattice vibrations, and one may think of a current of phonons moving down the temperature gradient. In each electron-phonon collision the phonon imparts its momentum to the electron with which it interacts, and in this way the electron-lattice interaction will cause electrons to drift along with the phonon current. The effect gives rise to an additional contribution to the thermoelectric e.m.f. and adequately accounts for the observations of Frederikse and also subsequent experimental work of Mooser & Woods (154) and Geballe & Hull (155, 156). ter Haar & Neaves (157) have extended the analysis to metals. While this phonon contribution has been discussed only in connection with the thermoelectric effects (Seebeck, Thomson), it will certainly also influence the thermomagnetic properties of metals and semiconductors.

Impurity band conduction.—According to the usual description of an impurity semiconductor (158), the resistivity and Hall coefficient should increase indefinitely as the temperature is lowered beneath that at which the activation energy of the impurity centers, donors or acceptors, is comparable to kT. The reason for this prediction is simply that with decreasing temperature the number of carriers in the conduction band for n-type semiconductors (valence band for p-type) will decrease exponentially, and resistivity and Hall coefficient depend on the reciprocal of the number of carriers present.

The earliest indications of the inadequacy of this theory came from the work of Hung & Gliessman (159, 160, 161) who measured Hall coefficient and resistivity of n and p-type germanium to helium temperatures. They found that contrary to the above predictions the Hall coefficient reached, at a certain low temperature, a maximum and then decreased quite sharply as the temperature was lowered further. At the temperature of the Hall maximum, the resistivity appeared to saturate, increasing only relatively slowly as the temperature was lowered. Also, the temperature at which the Hall maximum occurred increased with increasing impurity concentration. Hung interpreted these results by postulating that randomly distributed

impurity centers may give rise to a narrow band which can support conduction processes. In the succeeding years careful experimental work has shed additional light on the phenomenon. In particular, Fritzsche (162, 163) has shown by means of controlled experiments that the low temperature anomalies do not have their origin in surface effects, or other spurious causes, but are, indeed, bulk properties and are very sensitive to type and concentration of impurities. Impurity band conduction has now been observed in *n* and *p*-type germanium and silicon (164, 156, 162, 163) and also in *p*-type indium antimonide (165).

These observations have stimulated considerable theoretical work in an effort to understand and explain the phenomenon. It may appear surprising at first that impurity concentrations as low as 10^{16} and even less could give rise to significant broadening of impurity levels. One must remember, however, that the Bohr radius of an electron bound to a hydrogen-like impurity center is proportional to the dielectric constant and inversely proportional to the effective mass. Thus, in germanium, the effective Bohr radius of an electron bound to such a center is of the order of fifty times the classical Bohr radius. As a result, significant overlap of electronic wave functions centered on adjacent impurity atoms can occur for rather small impurity concentrations.

The first theoretical attempts to determine the width of impurity bands assumed that the impurity atoms were distributed on a regular sublattice within the semiconductor (166, 167, 168). This is certainly a poor assumption, and James & Ginzbarg (169), and more recently Aigrain (170), considered the situation in which impurity atoms are distributed at random. These workers found that a random distribution gives long tails to the narrow band that would have been the consequence of assuming a regular array. Consequently, the impurity band appears to overlap the usual conduction band already at rather low concentrations. It must be kept in mind, however, that the presence of impurities necessarily perturbs the conduction band so that a model of two overlapping bands of which one has the same features as in the absence of impurities is highly artificial and probably incorrect. At the present time the problem of impurity bands is still in its infant stage, as evidenced by the inability of existing models to account for many details of the low temperature anomalies in semiconductors. For example, the simple model of Hung leads to the conclusion that the Hall coefficient approaches, at very low temperatures, the same value as in the exhaustion range—the temperature range where all impurities are ionized although the semiconductor is still in the extrinsic region. In fact, the Hall coefficient generally saturates to a value appreciably different from the exhaustion value; in some cases the Hall coefficient does not saturate at all (162). Also, the resistivity does not saturate completely but rather continues to increase slowly with decreasing temperature (162). Attempts have been made to account for these features by considering bands formed from excited impurity levels (166, 167), but these attempts do not appear to be altogether

satisfactory. A most unusual behavior has been noted in *p*-type InSb. In this material, at a temperature slightly below that at which the Hall coefficient passes its maximum, the magnetoresistance reverses sign and is negative at all lower temperatures (165). This phenomenon is quite perplexing since one can show that for any reasonable band model the expression for magnetoresistance is positive definite. No explanation for the negative magnetoresistance, qualitative or quantitative, has yet been advanced.

Pressure dependence.—During the past few years the dependence of the properties of germanium and silicon on hydrostatic pressure has been scrutinized in a series of experiments. Measurements of resistivity of germanium (171, 172) showed that the energy gap between the valence and conduction bands increases with pressure at the rate of about 5.5×10^{-12} ev per dyne/cm.^{2} near room temperature and for pressures up to 15,000 kg./cm.^{2} These results are in good agreement with a number of related observations of which the most direct are changes in optical absorption edge with pressure (173). The deformation potential theory of lattice scattering (174) also indicates changes in energy gap of this magnitude. Recent careful work by Benedek *et al.* (175), who measured resistivity, Hall effect and magnetoresistance of *n*-type germanium and their pressure dependence at 0°C. shows that not only does the energy gap change with pressure, but the shape of the surfaces of constant energy in $\mathbf{k}$-space in the conduction band also are pressure sensitive, the energy ellipsoids becoming less prolate with increasing pressure. Further, the energy dependence of the lattice scattering relaxation time also appears to increase with pressure.

In silicon, application of high pressures causes a decrease in the energy gap at the rate of about -1.5×10^{-12} ev per dyne/cm.^{2} as evidenced by measurements of resistivity (176) and also changes of optical absorption with pressure (173).

Measurements of conductivity as a function of pressure in indium antimonide show that in this material the energy gap increases with pressure at the rate of about 15×10^{-12} ev per dyne/cm.^{2} (177, 178). The electron mobility appears to be approximately inversely proportional to the energy gap, whereas the hole mobility shows no significant pressure dependence. These results permit the inference that the conduction band minimum in InSb occurs at $\mathbf{k}=0$ but that the valence band has maxima away from the center of the Brillouin zone (178).

Impurity Levels

Addition of a small amount of the Group III elements in the periodic table such as boron, aluminum and gallium is known to produce a *p*-type semi-conductor whereas the addition of the Group V elements such as phosphorus, arsenic and antimony produces *n*-type specimens. These elements introduce impurity levels which lie about 0.01 ev above the valence band for *p*-type impurities, and 0.01 ev below the conduction band for *n*-type impurities. This effect can be understood in terms of a hydrogenic model

for the impurity center. Ionization energies computed on this basis (with the effective mass correction) agree well with the measured values. These impurities are assumed to occupy substitutional sites in the matrix.

Experimentally, the determination of the localized energy levels consist mostly of measuring the electrical resistivity and the Hall effect as a function of temperature. Experiments show that the hydrogenic model becomes inadequate when elements which do not belong to the Group III or V are added. For the case of doping by Zn, (179) the helium-like model is mildly successful in explaining the experimental value but the same model does not yield satisfactory values for Cu and Pt (179). Addition of gold in Ge was extensively studied by Dunlap (180). It was found that gold behaves as an acceptor in Ge and produces two levels, one at 0.15 ev above the valence band, the other 0.20 ev below the conduction band. Compatibility of this level scheme was confirmed by Newman (181). The implication of this model is that the specimen is either p- or n-type depending on the relative proportions of gold atoms and other normal donors and acceptors. These two levels are considered to be due to the two different ionization states of gold, namely Au^{-} and Au^{--}. In silicon, however, gold doping produces a donor level 0.33 ev above the valence band. [Taft & Horn (182), Newman (183)].

Impurity levels due to Cu in Ge were studied extensively and acceptor levels at 0.25 and 0.04 ev were found (179, 184 to 188). The doping effect of transition metals, Fe, Co, Ni and Mn in Ge was studied by Tyler, Newman & Woodbury (189, 190 to 195). These impurities were all found to be double-acceptor impurities. Recently a second level was found for Zn-doped Ge (196). No impurity levels were observed in Ge by the introduction of vanadium, tin and lead (195).

There has not been any theoretical work on impurity levels except for the hydrogenic model [Kohn & Luttinger (197)] which will be discussed in the following section.

Selected Theoretical Topics

We conclude the discussion by reviewing very briefly some of the con tributions to the theory of solids, particularly as they apply to the properties of germanium, silicon and other semiconductors. With this restriction it is possible to divide the material into two main groups, namely (*a*) spin-orbit coupling in band theory and (*b*) theory of impurity levels and motion of electrons in perturbed periodic lattices.

Spin-orbit coupling.—It has only been fairly recently that the influence of spin-orbit coupling in band theory has been investigated in some detail. The first calculations of the band structure of germanium (198), in which spin-orbit coupling was neglected, indicated that the valence band is triply degenerate at $\mathbf{k}=0$. However, only two distinct effective masses of holes were observed in cyclotron resonance experiments (199). Dresselhaus *et al.* (200) suggested that the valence bands are split by the spin-orbit interaction and that, in fact, the top of the valence band is only doubly degenerate,

corresponding to two $p_{3/2}$ orbitals, the band formed from the $p_{1/2}$ orbitals lying well below these. Further experimental evidence for the splitting comes from the structure of the infrared absorption spectrum of p-type germanium (122, 123, 124) which has already been mentioned.

A detailed discussion of spin-orbit coupling in band theory was given by Elliott (99, 201), who extended the group theoretical arguments of Bouckaert *et al.* (202) and of Herring (203) on the symmetry properties of energy bands in solids so as to include spin-orbit interaction. Elliott treated the simple, face-centered, and body-centered cubic, diamond, and the hexagonal close-packed lattices, giving character tables for the double space groups of these lattices. Parmenter (204) and Dresselhaus (205) have extended this work to include the zinc blende structure which is similar to that of diamond except that it lacks the inversion symmetry characteristic of the latter; hence the double degeneracy (including spin) imposed by the inversion symmetry at an arbitrary point in $\mathbf{k}$-space for diamond does not occur in zinc blende lattices, such as indium antimonide.

Before leaving this subject mention should be made of another phenomenon which finds its explanation in the interaction of electron spin with its orbital motion. The anomalous Hall effect of the ferromagnetic metals had been a mystery for decades (206). In these metals the Hall effect was found to increase from the normal value, $1/nec$, to a value orders of magnitude larger as the temperature was raised from liquid helium to the Curie temperature. At the Curie temperature the Hall coefficient was observed to decrease almost discontinuously to about $1/nec$. This phenomenon has been explained by Karplus & Luttinger (207) in terms of spin-orbit coupling of polarized electrons.

Electrons in perturbed periodic lattices.—The description of electrons in perturbed periodic lattices also has received considerable attention in recent years. This work was stimulated in large measure by the need to understand in detail the properties of electrons bound to impurity centers in semiconductors. Luttinger & Kohn (208), and concurrently Kittel & Mitchell (209), showed how the effective mass approximation (210, 211, 212) could be extended to treat more complicated situations than had previously been discussed, such as those in which the energy band minimum is not at the center of the Brillouin zone and those in which energy bands are degenerate at extrema; these cases are, of course, just the ones of interest in n and p-type germanium and silicon. These workers found that in the case of degenerate bands the usual Wannier equation cannot be used, and instead a set of coupled differential equations must be solved. These methods have been applied to the problem of the ground state and excited energy levels of hydrogen-like impurity centers in silicon and germanium (209, 213, 214, 197, 215). In the case of the ground state the effective mass approximation does not lead to good agreement with experimentally measured ionization energies, the discrepancy probably being due to failure of the approximation near the impurity center. The theoretical spectrum of the excited p-like

states, however, is in good agreement with measurements of Burstein, Picus & Henvis (216).

Attention is also directed to the work of Koster & Slater (217, 218, 219) and of Feuer (220) who have treated the problem of impurity states in solids especially in those situations which are relatively tractable analytically, such as the linear chain, with the view of ultimately extending the techniques to more realistic cases.

A problem closely related to that of localized electronic levels about impurities has been discussed recently by Montroll & Potts (221, 222), who investigated the effects of point defects on the vibrational spectrum of a crystal lattice. They found, in analogy to the bound electronic impurity states, that many defects give rise to vibrational modes which are localized about the defect and decay exponentially with distance from the imperfection. Besides perturbations due to point imperfections, perturbations arising from lack of order also have been investigated during the past year. The mathematical techniques for one dimensional problems have been discussed by Dyson (223) and by Landauer & Helland (224); Parmenter (225, 226, 227) has indicated suitable methods for handling three dimensional problems of similar nature.

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ISOTOPES[1]

By Joseph Silverman
Radiation Applications Incorporated, New York, New York
and
Karl Cohen
General Electric Company, Atomic Power Equipment Department, San José, California

Introduction.—As our experimental techniques become more refined, the physico-chemical differences of isotopes become more apparent, and the subject of isotopes in physical chemistry becomes almost coextensive with physical chemistry itself. The selection of topics for a brief review is thus necessarily arbitrary. An accurate knowledge of the atomic masses and an understanding of isotope effects on equilibrium phenomena and on reaction kinetics are obviously basic to analytical chemistry, the biological sciences, and isotope separation. Analytical techniques are included as much for their bearing on crosscomparison with nuclear transformations as for their basic interest to all researchers in the field. In isotope geology we have retained, not without some qualms, the traditional distinction between isotope abundance changes arising from nuclear phenomena and isotope abundance changes from physico-chemical causes. Only the latter are treated here.

Since last year's review omitted the subject of isotope separation in favor of a comprehensive review of isotope geology, we have brought the topic of separation up-to-date with literature references from 1954 as well as 1955. Outside of this field the review covers articles which appeared in the principal periodicals during 1955.

Instruments and Methods

The precise measurement of atomic masses has long been dominated by the mass spectrometer. In recent years nuclear transformation data have been used to obtain mass values of comparable precision and accuracy. More recently, the methods of microwave spectrometry have been applied to the precise determination of atomic masses. Although mass spectrometry also predominates in the measurement of isotopic ratios, here again competitive methods have been developed for some special problems.

Mass spectrometers.—Several laboratories reported a significant improvements in the construction and operational characteristics of their mass spectrometers. Mattauch and his co-workers (1) have refined their double-focussing instrument and have been able to achieve a resolving power of 100,000. Ogata & Matsuda (2) have recently constructed a double-focussing spectrometer with a dispersion coefficient of 9 cm. for a 1 per cent mass difference, and a maximum resolution of 500,000. Nier and his co-workers have also built a new double-focussing machine (3, 4); using a modulated mag-

[1] The survey of the literature pertaining to this review was completed in February, 1956.

netic field and fast electronic detection-amplification equipment, they have been able to observe adjacent peaks simultaneously on an oscilloscope with a maximum resolving power of 100,000 (5).

Another interesting development is the application of mass spectrometry to field-produced positive ions by Inghram & Gomer (6, 7, 8). The desorption of positive ions from surfaces by high electrostatic fields was first noted by Müller (9) who employed this phenomenon in the field ion microscope. Preliminary work indicates that this method favors the parent peaks and should therefore be especially useful in the analysis of gas mixtures, identification of free radicals, and related problems.

Microwave spectrometers.—In the field of microwave spectroscopy, the majority of the mass measurements have been made using the wave-guide gas absorption cell. Such instruments have been well described in two recent books (10, 11). The highest resolution with an instrument of this type has been achieved by the Columbia group (10, 12). For a typical molecule such as OCS at room temperature, absorption linewidths range from 70–100 kc., and absorption frequencies can be measured to an accuracy of 2 kc. in the 24,000 Mc. region.

The absorption linewidths in these instruments are determined mainly by Doppler broadening and molecular collisions with the walls. Romer & Dicke (13) have calculated that the collision effect can actually narrow the line in a gas cell with a large diameter-to-height ratio operated at low pressures. Because of the low gas pressures required, the improved resolution is gained at the expense of sensitivity. A severe loss in signal-to-noise ratio would result if these special gas cells were used in conjunction with conventional continuous absorption spectrometers. They obtained some improvement by employing the "pillbox" gas cell in their new pulse-induced emission spectrometer (14) in which gas molecules are excited by short pulses of microwave power to states from which they emit inherent spontaneous radiation. The 1.25 cm. inversion transition in ammonia was thus observed and lines $\frac{1}{4}$ of the normal Doppler width of 73 kc. obtained. The method has not yet been applied to mass determination.

Gordon, Zeiger, & Townes (15) have devised a microwave spectrometer with an even higher resolution; they report a line width of 6–8 kc. for the ammonia inversion spectrum. In their instrument, called the maser, a molecular beam is fed into a chamber in which a highly nonuniform electrostatic field selectively focusses molecules in some states and defocusses the others. The molecules in the selected states enter a microwave cavity tuned to a frequency corresponding to an allowable transition to a lower state. The radiation field in the cavity induces the transitions, thereby increasing the output radiation power. While no mass measurements have been made with the maser, such application may arise in the near future.

Isotopic abundance.—Techniques for measuring isotope ratios by spectroscopic methods have been reported. Kluyver (16) has developed a relatively

simple infrared analyzer with which he has been able to measure C^{13} abundance in 20 mg. of CO_2 to within 0.005 atom per cent C^{13}, and N^{15} abundance in 8 mg. of N_2O within 0.015 atom per cent N^{15} in the region of their natural abundance. Hürzeler & Hostettler (17) have an improved spectroscopic micromethod for the N^{15}/N^{14} ratio, using the 3159 A. line of $N^{14}N^{14}$ and the 3162 A. line of $N^{14}N^{15}$ for comparison. They find that they can make precise measurements with samples as small as 20 μg. and that the method is less sensitive to impurities than mass spectrometry.

Gaunt (18) has reported on infra-red methods of determining the D content of deuterated water samples. For samples with low D content, the 3.98 μ stretching band of OD is measured; in the 50 per cent region, he uses the 1.445 μ H_2O band; and at very high deuterium concentrations he uses the 2.946 μ band of HOD.

Collins & Ropp (19) have studied the accuracy obtained in the Van Slyke combustion and radioassay of C^{14} compounds, a method used at Oak Ridge in the study of isotope effects. Although the method is quite reproducible, it was not certain whether the combustion is quantitatively complete. They prepared a series of tagged carbon compounds from the same C^{14} sample by reactions which involved atoms well removed from the labelled positions. Consequently the molar activity in all the synthesized compounds were presumably identical. Subsequent combustion and radioassay gave the same molar activity for each of the compounds, indicating that the Van Slyke combustion is complete.

Atomic Mass Measurements

In the past two years there has been a concerted effort to reconcile the mass data from nuclear physics and microwave spectroscopy with those of mass spectrometry.

Nuclear reactions.—Several compilations of nuclear transformation data were published which are of potential importance in mass determinations: Briggs (20) summarized the data on the energies of natural alpha particles; Asaro & Perlman (21) covered the alpha disintegration energies of the heavy elements; King (22) presented a table of total disintegration energies; Robinson & Fink (23) gave a summary of the data on electron capture transitions; Ajzenberg & Lauritsen (24) summarized information on the energy levels and mass defects of the nuclei up through $Z=10$; Endt & Kluyver (25) presented similar data for nuclei up through $Z=20$; and Van Patter & Whaling (26) tabulated total nuclear disintegration energies. From such information, Wapstra (27) carefully and critically computed isotopic masses up through $A=33$; for the higher masses, he used data from all the techniques of mass measurement. Drummond (28, 29) obtained the masses of 76 nuclei up to $A=34$ from combined nuclear reaction data and mass spectrometer doublets.

Microwave spectroscopy.—In 1954, the measurements of mass differences and mass difference ratios by microwave techniques were reviewed by Gesch-

wind, Gunther-Mohr & Townes (30). Since then some additional information has been published in this field.

Rosenblum & Nethercot (31) determined the T/D mass ratio from measurements on TI and TBr, and older spectroscopic data. Burrus *et al.* (32) also measured the rotational spectrum of TBr and thereby obtained a T/D value. All the microwave results are in close agreement with each other and with the value derived from nuclear reaction data. Rosenblum & Nethercot point out that this agreement is fortuitous since there may be significant corrections arising from electron effects (particularly L-uncoupling) which they were unable to evaluate with adequate precision.

Mockler & Bird (33) reported high precision values for C^{12}/C^{13}, S^{32}/S^{33}, and S^{32}/S^{34} based on experiments on CS; their results do not agree with nuclear reaction values. Although he has high regard for the experimental data in (33), Geschwind (34) observed that the contributions to the molecular moments of inertia arising from the spacial distribution and motion of the electrons were not taken into account in calculating the mass ratios. An accurate estimate of the electronic correction could be made if the magnetic moment of CS were known. Geschwind calculated the magnetic moment of CS by assuming that the difference in the carbon ratios obtained by the two methods is equal to the correction term. He then used the calculated value to correct the sulfur ratios. The revised microwave mass ratios are in good agreement with the nuclear values. Independent measurements of the magnetic moment are now in order.

Honig *et al.* (35) measured the microwave spectra of several alkali halides and obtained the following mass ratios: Cl^{35}/Cl^{37}, K^{39}/K^{41}, Br^{79}/Br^{81}, and Rb^{85}/Rb^{87}; the results agree with mass spectroscopic and nuclear values. Two papers by Aamodt & Fletcher (36, 37) appeared which give mass difference ratios from measurements on polyatomic molecules: $(Cl^{36}—Cl^{35})/(Cl^{37}—Cl^{36})$ from CH_3Cl, and $(Se^{75}—Se^{76})/(Se^{75}—Se^{80})$ from OCSe.

Mass spectrometry.—In the field of mass spectrometry, two comprehensive compilations were presented in 1954: a critical compilation of atomic masses by Nier (38) which later appeared in (39); and an article by Duckworth, Hogg, & Pennington (40) summarizing atomic mass difference data by the doublet method, and the mass values published by the Brookhaven mass synchrometer group. In 1955, relatively few new data were published: Kerr, Duckworth *et al.* reported their attempts to resolve the discrepancies in the Cu-Ge region (41, 42) and the Minnesota group announced tentative values for H, D, C^{12}, and S^{32} (43).

Discrepancies.—An intercomparison of mass determinations by nuclear methods, microwave spectroscopy, and mass spectrometry yields, for the most part, excellent agreement, but there are still important areas of disagreement.

The problem of the C^{12} mass is still unresolved. Mattauch & Bieri (44) published an M-A value of 3823.1 ± 3.3 μM.U. in 1954. The Minnesota group

previously reported a value about 20 μM.U. units higher, but their new tentative value of 3817.4 ± 1.8 is almost in agreement with the German value (44). At a recent conference on mass spectrometry, Smith announced tentative results on the mass synchrometer that also agree with this value (45). Still to be heard from on this matter among the mass spectrometer specialists are Ogata & Matsuda (46) who published a higher value in 1953, and Ewald who published a lower value in 1951 (47). Wapstra's analysis of nuclear reaction data gives a value of 3803 ± 5 which conflicts with the new cluster of mass spectrometer data but is in agreement with Ewald's work.

The other important area of difficulty is the Cu—Ge region. Both Wapstra (27) and Kerr *et al.* (41) suggested that several discrepancies would be resolved if the mass spectrometer value for the Ni isotopes were 0.6 m.M.U. higher. The latter group also pointed out conflicts which appeared to revolve around the Zn isotopes. Upon further experimental investigation of these isotopes by the mass doublet method, Kerr *et al.* (42) concluded that the previous mass spectrometer values for Zn^{64} and Zn^{66} were too high by 0.4 m.M.U., and that acceptance of the new values would bring about agreement. The zinc values were obtained by a method which depends ultimately on the disputed C^{12} value of Mattauch & Bieri (44) and may therefore be subject to a small absolute error. Also the precision of the new measurements is admittedly somewhat low. Apparently more work is needed in this region.

Relative Abundance and Isotope Geochemistry

Senftle & Bracken (48) examined the possibility of isotope fractionation by diffusion as a factor in geology. They conclude it can occur and is most likely to be observed in trace elements deposited by diffusion.

Weston (49) computed the D/H equilibrium between water and ice. He calculated $(D/H)_s/(D/H)_l = K = 1.0192 \pm 0.0002$ at $T = 0°C.$, and $d \log K/dT = -6 \times 10^{-6}$ approximately. Sea water has the same equilibrium curve as fresh water, but the applicable value of K is of course less, corresponding to the lower freezing temperature. In rapid freezing we may have a situation like a Rayleigh distillation, with each layer of ice successively equilibrated with lighter water. Under these circumstances significant changes of deuterium content would be expected.

Friedman (50) measured the D/H ratio of water in specimens of tektite. It is about 15 per cent less than that of average sea water; the small water content is presumably of meteoritic origin. Knop (51) reported on the deuterium content of a large number of natural and industrial waters in Yugoslavia.

The experiments of Wagner & Pelz (136, 137) confirm the observation of Cameron (52) that the Li^7/Li^6 ratio varies readily when recrystallized as the carbonate. Gillieson & Thorne (53) succeeded in reconciling the spectroisotopic measurements of the Li^7/Li^6 abundance ratio with the mass spectrometric results by taking into account the Doppler effect. The Doppler broad-

ening of the spectral lines gives the relation $\int I(\upsilon)d\upsilon = I_{max}1.772(\upsilon_0/c)(2\ RT/M)^{1/2}$; hence the ratio $I_{max}(Li^7)/I_{max}(Li^6)$ should be multiplied by $(6/7)^{1/2}$ to get the true abundance. They found the spectro-isotopic ratio of the peak intensities for a particular Li_2SO_4 sample was 13.5 ± 0.3. The corrected abundance ratio is then 12.5 ± 0.3, in agreement with a preliminary mass spectrometric measurement on the same sample of 12.2 ± 0.1, and within Cameron's (52) range of values of 12.4 to 12.9. These results go far towards clearing up the previously unsatisfactory situation on lithium abundances. Gillieson & Thorne point out that an analogous correction will be significant for other elements, particularly the light ones.

Arnold & Ali Al-Salih (54) searched for and found cosmic ray produced 53-day Be^7 in rainwater. It is expected that it will be useful in the study of particle movement in the upper atmosphere.

Jeffery *et al.* (55) investigated the C^{13} abundance of Australian limestones and coals. Cyclic trends in the C^{13} abundance ratio are tentatively correlated with periods of net carbon fixation or release, the biosphere being low in heavy carbon at the end of a fixation period. Landergren (56), continuing his work on alum shales, reports the C^{13}/C^{12} ratios in organic carbon and in carbonate carbon were not affected by thermal metamorphism.

The use of C^{14} for dating has become as widespread as routine tracer work, and standard methods of reporting dating results from over a dozen laboratories have been proposed. A review of some of the archeological results is given by Libby (57).

Ingerson (58) in a review article on the use of the O^{16}/O^{18} ratios to determine deposition temperatures of carbonates, introduces some new data of C. Emiliani on Globigerina from deep-sea cores. Temperature maxima and minima are found which correspond to glacial climatic periods.

Ault (59) found the S^{32}/S^{34} ratio in a number of sulfides to be consistent with the source of the sulfur (meteoritic or sedimentary) but independent of the mineral species. The constancy of the sulfur isotope abundances in Mississippi Valley type lead ores indicates that variations in the lead isotope abundances are not caused by isotope fractionation.

Wetherill, Aldrich & Davis (60) tested the usefulness of the K^{40}—A^{40} method of dating rocks by examining the retention of argon in feldspars and micas from the same rock. Significant losses of argon were evident in the feldspars.

Gast (61) found the predicted Sr^{87}/Sr^{88} increase in limestones containing rubidium was much greater than he observed, but Aldrich *et al.* (62) using an isotope dilution technique on micas from eight granites continue to observe very marked alterations from the natural abundance ratio.

The interesting subject of the Pb^{207}/Pb^{206} ages, based on the amount of radiogenic lead isotopes, is remote from physical chemical considerations and is consequently not discussed here. It is reviewed in an article by Patterson, Tilton & Inghram (63).

A second naturally occurring isotope of tantalum was observed by White, Collins & Rourke (64). The abundance of this isotope, Ta^{180}, is 0.0123 $\pm$0.0003 per cent.

Isotope Separation

Heavy water separation.—A monograph on the production of heavy water in the National Nuclear Energy Series (65) reviews war-time developments in the United States. The first part of the volume gives an engineering account of the Trail, British Columbia combined catalytic exchange and electrolytic plant, the Morgantown, West Virginia water distillation plant, and brief analyses of other proposed methods. Part II describes the experimental investigations which supported or condemned the various methods. There is considerable information on the development of catalysts for H_2—H_2O(l) and H_2—H_2O(g) exchange. A glass pilot plant for H_2—H_2O(g) exchange is described in detail. Experimental data and design considerations on dual temperature cycles using mercaptan-H_2O, NH_3—H_2O—H_2, and cyclohexane-benzene-H_2 are given, and on water distillation using an additional component as a separating agent. Benedict (66) brought this material up-to-date with an economic and engineering evaluation of D_2 production by distillation of H_2, distillation and electrolysis of H_2O, H_2—H_2O(g) simple exchange, and dual temperature cycles using H_2O—H_2, H_2O—H_2S and NH_3—H_2.

A flow sheet and model of a hydrogen distillation deuterium plant, under construction in France, was exhibited at the United Nations Conference at Geneva, as were plans for a New Zealand distillation plant using geothermal steam (since discontinued). A new distillation column packing, "Spraypak," had been developed for this purpose (67). Wladimirsky *et al.* (68) use 99.56 per cent electrolytic D_2O as the starting point for preparation of samples of pure D_2O by rectification. Baertschi & Kuhn (69) describe composite columns made up of a number of packed columns a few centimeters in diameter combined in parallel in one vessel. Wire gauze rings or helices are used as packing. The multiplication of small columns avoids the loss of efficiency which occurs when scaling up to large diameters. The concentration range of D envisaged is 0.1–1 per cent to 99.8 per cent. The design equations for the D_2O distillation process are discussed by Dostrovsky & Lehrer (70). Savic *et al.* (71) reported on the efficiency of platinum and transition element oxides as catalysts for promoting the exchange of H_2—H_2O(g).

Chemical exchange.—A useful bibliography on isotope separation and isotopic exchange reactions covering the 1907–1953 literature of B, C, Cl, H, Fe, Li, N, O, S and U, with incomplete references to other elements, is available from the U. S. Atomic Energy Commission (72).

Taylor and co-workers investigated the concentration of N^{15} using the oxides of nitrogen (73 to 76). The first experiments contacted NO with NO_2 in a thermal diffusion column. The descending cold stream is principally NO_2, while the ascending hot stream is $NO+O_2$. Roughly half the separation

could be attributed to the thermal diffusion effect, and half to chemical exchange. Later they found a chemical exchange factor of 1.045 between NO and concentrated HNO_3, which compares with 1.023 for the NH_3—NH_4NO_3 system in common use. A two-column cascade, the first column 5.5 meters long and 2.5 cm. i.d., the second 5.5 meters long and 0.9 cm. i.d., both packed with stainless steel helices, permitted the production of about 0.5 gm. per day of nitrogen analyzing over 99 per cent N^{15}.

The U.S.S.R. Geneva exhibit showed a model of a plant producing 10 kg. per year of NH_4NO_3 containing 50 per cent N^{15} by NH_3—NH_4NO_3 exchange. The first stage is an almost horizontal unit in which ten to fifteenfold enrichment is obtained; the second is a vertical column (77). Marchetti (78) discussed the design of a chemical exchange column.

Distillation.—The U.S.S.R. (77) described a H_2O distillation cascade producing 1.5 kg. of H_2O per year containing 50 per cent O^{18}, starting from 1.0–1.5 per cent H_2O^{18} feed. It is comprised of three columns varying in diameter from 2–5 cm. and containing fine-grained stainless steel packing. The plate height is 1–2.5 cm.; 2500 plates are needed. The columns are vacuum jacketed.

The U.S.S.R. produces B^{10} by distilling BF_3 at −103°C. A 12 meter column with 570 theoretical plates contains constantan rings (1.2 mm. diameter, 0.25 mm. wire) and produces 4.5 kg. per year of BF_3 containing 83 per cent B^{10}.

Thermal diffusion (gases).—Thermal diffusion columns continue to be a popular means for producing experimental quantities of separated isotopes. A good deal of research on thermal diffusion factors is being carried out because of their sensitivity to intermolecular forces.

Mason (79 to 82), Saxena & Srivastava (83) and Madan (84) have evaluated collision integrals for exp-six and 12–6 intermolecular potentials, and introduced these into Chapman & Cowling's first and second approximation, and Kihara's (85) first approximation to the thermal diffusion factor. The results were compared with experiment with reasonably good agreement. Saxena (86) and Holleran (87) interrelated the diffusion coefficient, the viscosity and the thermal diffusion factor using higher approximations, and compared the results with experiment. Clusius & Huber (88) devised a new apparatus for determination of the thermal diffusion factors over relatively narrow temperature ranges. A number of vertical tubes are arranged with the tops at temperature T_1 and the bottoms at T_2. They are connected in series, the top of one to the bottom of the next, by capillaries through which gas is pulsed back and forth. At equilibrium, if q is the separation factor in one tube, then the separation of n tubes becomes

$$q^n = (T_1/T_2)^{n\alpha}$$

from which the thermal diffusion factor, α, is determined. The results on CO_2—H_2 mixtures agree with Kihara's formula for α, using 12-6 potentials,

but not with Chapman & Cowling's first approximation. The same authors (89) investigated Ne^{20}—NH_3, Ne^{22}—NH_3 and Ne^{20}—ND_3 mixtures and confirmed the reality of a reversal in sign of α, as indeed theory predicts. Clusius and his co-workers (90, 91, 92) have described successful separation in high purity of Ne^{21} from Ne^{20} and Ne^{22}, using deuteromethanes as an auxiliary gas; Xe^{136}; and C^{13} from methane. Equilibrating successive columns by displacing gas back and forth in capillary tubing is a significant improvement in technique used by the Clusius laboratory. McMillan (93) reported the enrichment of B^{10} in BF_3 by thermal diffusion; and Horibe & Nishizawa (94) describe a three-stage cascade of seven tubes separating C^{13} in methane. A hot-wire column to concentrate tritium is described by Almqvist, Allen & Sanders (95).

Hengevoss & Fleischmann (96) and David (97) experimented on the validity of the thermal diffusion equations and found deviations at high throughputs. Air was used as a test gas. De Vries (98) considered the problem of enriching small quantities of materials from a thermal diffusion column.

Thermal diffusion (liquids).—Efforts to understand the thermal diffusion effect in liquids have continued. Most of the experimental work has been on non-isotopic mixtures since these are easier to measure, if not to explain. Drickamer and co-workers (99 to 103) investigated the pressure effect, both theoretically and experimentally. In a later paper (104) they revise their earlier formulation and interpret diffusion factors in terms of energies of vaporization and a "packing efficiency" which is not clearly defined. Korsching (105) describes a new apparatus for measuring the thermal diffusion factor in liquids using only 0.25 $cm.^3$ of sample. Agreement between his and previously reported measurements on pairs of organic liquids is mediocre. Alexander (106) considers that the liquid "lattice" is moving relative to the center of gravity of a diffusing liquid because of reaction to the diffusion stream. By referring molecular displacements to the coordinates of the moving lattice, it is possible to take account of differing activation energies for each molecular species. The ideas are subsequently applied to solutions of electrolytes. A recent paper by Alexander & Dreyer (107) reports on the separation of Cl^{37} from Cl^{35} in trichloroethylene. They find $D = 1.8 \times 10^{-5}$ $cm.^2/sec.$, and $\alpha = 0.01$. One separating unit is used to get three times 1.15 per cent enrichment by accumulating the products of the first stage.

Electrolytic migration.—Klemm (108) described an apparatus for separating Li^6 from Li^7 by electrolysis of molten LiCl. Li^6 has a 2.2 per cent greater migration velocity than Li^7. Li^6 to 20 per cent and Li^7 to 99.8–99.9 per cent purity is achieved. Lundén & Berne (109) found a difference in the migration velocities of Cu^{63} and Cu^{65} in $Cu\,Cl_2$ of 0.25 per cent. The mass effect,

$$\mu = m\Delta v/v\Delta m = -0.080,$$

is in good agreement with the rule,

$$\mu = -0.15(1 + 0.476\, m_+/m_-)^{-1}$$

proposed earlier by Klemm. However later work on chlorine in lead chloride ($\mu = -0.052$) and potassium in potassium nitrate ($\mu = 0.036$) are in serious disagreement with the rule [Klemm & Lundén (110), Lundén, Reuterswärd & Sjöberg (111)]. Haeffner (112) found that passing a current of 2000 amp./cm.^{2} through mercury concentrates the heavy isotopes at the cathode. The separation factor is 1.022 for a 1 per cent mass difference. Nief & Roth (113) found a change of about 13 per cent in the same direction in the Ga^{71}/Ga^{69} abundance ratios, with a current density of 8000 amp./cm.^{2}. Lundén *et al.* (114) passed 2900 amp./cm.^{2} through molten K and increased K^{41}: K^{39} at the cathode by a factor of 1.12. Klemm (115) explains the effect in terms of mobile and immobile ionic states, whose ratio is isotopically invariant. The mobile state interacts strongly with the electrons and hence the lighter and more mobile isotope moves preferentially to the anode. The use of molten salts seems more practical since in metals an equivalent difference in isotope drift velocities requires 10^4 times the power.

Bonnin, Chemla & Sue measured the differences in ionic mobilities between Na^{24} and Na^{22} by diffusing them on moving paper against a high electric field (116). Chemla & Bonnin (117) did a similar experiment using molten $NaNO_3$—KNO_3 on asbestos. The difference in mobilities was 3 per cent in the former experiment and 1 per cent in the latter.

Electromagnetic separators and other gaseous ion devices.—Mass spectrographs continue to be used routinely to produce stable isotopes in small quantities. Keim (118) reviewed the production of stable isotopes at Oak Ridge, and in a companion paper Allen *et al.* (119) reviewed the production at Harwell. Other reports by Keim appear as occasional papers distributed by the U.S. Atomic Energy Commission; references may be found in *Nuclear Science Abstracts.*

The French electromagnetic isotope separator is described by Bernas (120). Koch & Nielsen (121) describe the Copenhagen separator, which is very similar to the ones in Stockholm, Uppsala, and Goteberg. The Stockholm instrument is described by Thulin (122, 123). The ion source and anti-contamination circuit of the Amsterdam separator are described in great detail by Kistemaker, Schutten, Zilverschoon, and de Vries (124, 125).

Slepian describes unsuccessful results on an ionic centrifuge (126) and mentions a modification in the method of drawing ions from the ion source which he believes will make a radical improvement (127). Hofmann & Walcher developed the theory for a time-of-flight separator which is to be space-charge independent (128). An all-electrical ion separating device has been developed by Paul & Raether (129). A 1000 volt 2–3 Mc. quadrupole field is established by means of four parallel copper tubes in a close array; each tube is 50 cm. long and has a diameter of 1 cm. It can be shown that applying a supplementary static field to this system permits stable orbits for ions of a narrow mass range only. The velocity of the ions does not effect their stability.

The device is used as a filter to separate isotopes. Using a 100 v. ion accelerating field, a fairly sharp separation of the Rb^{85}—Rb^{87} isotopes with 10 per cent of the ions passing through can be achieved. Advantages claimed for this system, beside the absence of magnets, are low voltages, independence of ion velocities, large area of utilizable path (and hence low space-charge effects), and ready adaptability to mass production with reduced power losses by expansion to a lattice. Experiments reported to date give no production runs.

Centrifuges.—Hertz & Nann find that a temperature difference between the end-caps will induce counter-current circulation in the centrifuge (130, 131). Using xenon, an axial concentration gradient is established, showing an overall separation factor corresponding to 5 radial equilibrium ratios. Equilibrium time variations are in accordance with theoretical expectations, assuming the axial velocity is proportional to the imposed temperature difference.

Diffusion methods.—Haul (132) found that diffusion of oxygen through a porous plug at 77°K. gave separation factors greater than calculated for pure Knudsen flow. Heymann & Kistemaker (133) described an apparatus for separation by diffusion through a condensable vapor. The vapor source and condenser are arranged as concentric vertical cylinders, and counter-current cascading is achieved by vertical convection of the gas being separated. Ne is separated in H_2O, and A in methanol. A vapor diffusion unit based on Hertz' porous tube diffuser incorporating a nickel filter with 100 μ openings, was shown and briefly described at the Russian exhibit at Geneva (77). The apparatus was designed to separate BF_3 at 50 mm. Hg using mercury as the auxiliary gas. The reported separation factor (1.016) is close to the theoretical value. An advanced model designed to operate at atmospheric pressure, using a nickel hydrodynamic barrier with 10–15 μ openings, and adapted to cascading, was also shown. It was stated that isotopes of C, Ne and A were separated in it, using H_2O, heptane and xylene as auxiliaries. From a scientific standpoint this information leaves much to be desired, and is of interest only as a first disclosure of an obviously substantial development.

Becker, Bier & Burghoff (134) described a new method of separation based on the use of a Laval nozzle developed to produce a high intensity molecular beam (135). Gas is expanded a few hundred-fold to a Mach number of 4 or 5. The jetted gas is collimated and has a narrow velocity distribution (half-width is about half that of an ordinary molecular beam). The beam, once out of the jet, tends to broaden and resume a normal velocity distribution by collisions. In an isotope mixture the light isotope does this faster and hence is concentrated at the outer portion of the jet. Becker *et al.* report that separation factors approximate those in a Hertz diffusion unit. The use of nozzles rather than a porous membrane is believed to result in more reliable apparatus with greater throughputs. However, it is unlikely that a method that expends so much energy in gas expansion and requires all the gas to be pumped at 0.1 mm. Hg can be economical for isotope separation.

Miscellaneous methods.—Precipitation of Li_2CO_3 15 or 20 times from chloride solutions showed enrichment of Li^7 with a simple process factor of 1.0069 [Wagner, Pelz & Higatsberger (136), Wagner & Pelz (137)]. Some implications of this result are discussed above in Isotope Geology. Ion exchange absorption columns have been used for laboratory scale enrichment of Ca^{45}, N^{16}, and Na^{24}—Na^{22} (138, 139, 140). Rohrman *et al.* (141) reported unsatisfactory results on isotope separation of heavy metals by electrolysis although an effect was observed with nickel.

Bankoff & Lyon (142) report the results of a theoretical study of isotope separation by ultrasonic waves. They expect negligible effects.

Isotope Effects in Equilibrium Phenomena

Most of the work published in 1955 in this field proceeded along now familiar lines. The thermodynamic properties of several isotopic compounds were determined by theoretical calculations and spectroscopic measurements. Similarly isotope effects on the equilibrium constants of various chemical and physical systems were measured and calculated. Some papers shed new light on old problems. Others will undoubtedly spark new controversies.

Stranks (143) measured the equilibrium constants for the reactions:

$$Co(en)_2CO_3^+ + HC^{14}O_3^- \rightleftharpoons Co(en)_2C^{14}O_3^+ + HCO_3^-$$

and

$$Co(NH_3)_5CO_3^+ + HC^{14}O_3^- \rightleftharpoons Co(NH_3)_5C^{14}O_3^+ + HCO_3^-.$$

The observed constants are 0.9810 ± 0.0053 and 1.000 ± 0.005 at 0°C., and the heats of reaction are -36.9 ± 9.3 and 0.1 ± 3.2 cal./mole respectively. Yankwich & McNamara (144) have previously reported that the equilibrium constants for the C^{13} and C^{14} exchange reactions with $Co(NH_3)_4CO_3^+$ are unity, which is almost in agreement with Stranks' results. The $HC^{14}O_3^-$ exchange with $Co(NH_3)_4CO_3^+$ has also been previously reported by Stranks & Harris (145); their equilibrium constant has the surprisingly low value of 0.8746 ± 0.0057 and the heat of reaction is -140 ± 25 cal./mole. Stranks (143) explains the differences in isotope effects in terms of an exchange mechanism involving a bicarbonate-complexed intermediate; the intermediates for the ethylene diamine and the tetrammine complexes each contain a molecule of H_2O while the pentammine complex does not. Theoretical calculations based on an approximate model give reasonable agreement with the observed results and indicate that small variations in the bond strengths of the coordinated complexes can lead to relatively large isotope effects.

Saito & Lazard (146) also measured the $Co(NH_3)_4CO_3^+$ exchange. They used normal C as well as samples labelled separately and simultaneously with C^{13} and C^{14}. Like Stranks & Harris (145) they observed an apparent equilibrium constant of 0.89 at room temperature for the C^{14} tracer experiments;

but using the normal isotopic mixture, they obtained a value of 1.00 for the C^{13} exchange, instead of the expected 0.95. From these data and the results of several auxiliary tests they concluded that the true equilibrium constant is unity and that the apparent effect arises from an impurity which they were unable to identify. Although Saito & Lazard present strong support for their conclusions, additional investigations on this problem can be expected.

Stranks (147) also measured the equilibrium constant for the exchange reaction

$$C^{14}O + COCl_2 \rightleftharpoons CO + C^{14}OCl_2$$

as a function of temperature. The results ranged from 1.1078 at 0°C. to 1.0085 at 500°C. Calculations based on the statistical mechanical method of Urey fit the observed values rather well. Stranks attributes the anomalous C^{14} effects reported for the decarboxylation of acids to experimental errors (148, 149, 150).

Bigeleisen (151) issued the first of a new series of papers on the statistical mechanics of isotopic systems with small quantum corrections, i.e. systems in which the $u^2/24$ approximation obtains (152). He shows that the differences in the thermodynamic properties of two isotopic species depends upon the difference in the reciprocal masses of the atoms in the molecule, and are therefore dependent solely upon the masses of the isotopically substituted atoms. This theorem provides a rigorous proof of the well-known rule of the geometric mean for gaseous molecules. The theorem also shows that the partition function ratio for a pair of doubly-labelled molecules, such as $N^{15}D_3/N^{15}H_3$, is equal to the ratio for the singly-labelled pair, $N^{14}D_3/N^{14}H_3$.

Bigeleisen & Kerr (153) conducted vapor pressure measurements with HT at 20.3°K. to test the applicability of the rule of the geometric mean. According to the rule, HT and D_2 should have appreciable differences in vapor pressure. This is in contradiction to earlier Rayleigh distillation experiments, an empirical treatment of the vapor pressures of isotopic hydrogen molecules, and a calculation based on the application of quantum corrections to the law of corresponding states. Bigeleisen and Kerr found a marked difference. Their P_{H_2}/P_{HT} ratio is 2.0 and the P_{H_2}/P_{D_2} ratio previously measured by Hoge & Arnold (154) is 2.89. Bigeleisen's theoretical calculation for the P_{H_2}/P_{HT} ratio is 2.03–2.10 thus supporting the validity of the rule for this system.

Thompson & Schaeffer (155) measured the equilibrium constant for the reaction

$$H_2 + D_2 \rightleftharpoons 2HD$$

at 20°C. and at 110–240 mm. Hg. Using Po^{210} alphas and 2 Mev electrons to induce equilibration, they obtained values which were in excellent agreement with constants obtained from control samples in which equilibrium was

achieved by catalysis with Ni. Their mean value for the radiation-induced equilibrium constant is 3.23 ± 0.07 which is in good agreement with theoretical expectations. They conclude that radiation effects cannot account for the 12 per cent discrepancy between the theoretical constant and the value reported by Mattraw, Pachucki & Dorfman (156). They also obtained the G values for the radiation-induced equilibration reactions: 9×10^3 for the 2 Mev electrons, and 4×10^4 for the Po^{210} alphas.

Lachowicz, Newitt & Weale (157) measured the solubility of D_2 and H_2 in n-heptane at 25–50°C. and 50–300 atm. From the results, they calculated the Kuenen solubility coefficients and the partial molar volumes of the dissolved gases. The partial molar volume of H_2 is observed to be less than that of D_2; the authors attribute this to the lower compressibility of H_2.

Abraham & Flotow (158) measured the standard heats of formation of UH_3, UD_3, and UT_3, using an adiabatic calorimeter. Their reported values are $-30{,}352 \pm 30$, $-31{,}021 \pm 30$, and $-31{,}141 \pm 50$ cal./mole respectively.

Mulford & Sturdy (159) obtained equilibrium pressure-temperature curves for the Pu—H_2 and Pu—D_2 systems. From these they calculated the following vapor pressure equations:

$$\log P_{PuH_3}\ (\text{mm. Hg}) = 10.01 \pm 0.32 - (8165 \pm 263)/T \qquad 400 < T < 800°K.$$
$$\log P_{PuD_3}\ (\text{mm. Hg}) = 9.71 \pm 0.19 - (7761 \pm 151)/T \qquad 600 < T < 800°K.$$

The heats of formation are -37.4 ± 1.2 and -35.5 ± 0.7 kcal./mole respectively.

Potter, Bender & Ritter (160) measured the vapor phase association of CD_3COOD at 80–170°C. and 100–800 mm. Hg. They interpret the data in terms of a mixture of monomer, dimer, and trimer. The heats of dimerization are given as -14.1 and -23.2 kcal./mole. They recomputed the data of Ritter & Simons (161) for CH_3COOH on a similar basis and obtained -13.7 and -22.8 kcal./mole for the corresponding values. The difference between the heats of dimerization of the two species is attributed to the difference in the zero point vibration energies.

The calculation of ideal gas thermodynamic functions using the high speed machine computer at the National Bureau of Standards was briefly described in the previous review. This work has been extended by Haar & Friedman (162) to the diatomic free radicals of the isotopic hydrides of O and S. Similar computations are reported for the isotopic hydrogen sulfides (163).

Several papers were published in which the detailed thermodynamic properties of isotopic compounds were derived from spectroscopic and other supporting experimental data: Giguére & Liu (164) on H_2O_2 and D_2O_2; Palm & Kilpatrick (165) on HNO_3 and DNO_3; Weissman *et al.* (166) on CD_3Br and CH_3Br; Dowling (167) on $BrCDH_2$ and $BrCD_2H$; and Polo *et al.* (168) on $CHBrCl_2$ and $CDBrCl_2$.

Isotope Effects in Chemical Kinetics

Chemical kinetics continues to provide one of the most fertile fields for the application of the isotope effect. Such applications have not only given valuable information for the elucidation of reaction mechanisms and molecular structure, but they have also proved to be of great importance in the study of fundamental theories of kinetics.

Polanyi (170) examined the absolute rate calculations by Eyring and co-workers on the series of eight isotopic exchange reactions between H and H_2. He found that the rate constants of only two reactions, $H+H_2$, and $D+D_2$ are independent observations; the rest of the "experimental" constants were calculated from ratios of rate constants by applying collision theory. Therefore these data fail to provide a real test of Eyring's method. Recently Steacie and his co-workers published experimental data on the four exchange reactions between CH_3 and the isotopes of H_2, and the four similar exchange reactions involving CD_3. Polanyi used this set of independent observations to test the Eyring rate theory. The calculations resulted in a series of rate constants, the largest of which is 40 times the smallest. The observed maximum-to-minimum ratio is 7:1. The difficulty appears to lie in the calculation of the energy surface. The Eyring surface, which is constructed from Morse functions, is asymmetric and contains a potential energy basin indicating the existence of stable H_3 or CH_5. Polanyi reconstructed the surface introducing a coulombic contribution sufficient to make the basin vanish. Zero-point energies derived from this calibrated surface lead to relative rate constants in fair agreement with the eight observed values.

Attempts to calculate the kinetics of the reaction of Cl_2 with the isotopic forms of H_2 from purely a priori considerations have yielded results which do not agree with experiment. Bigeleisen & Wolfsberg (171) therefore attempted it by a semi-empirical method. Two transition state complexes of the form H_2Cl were considered, a linear structure and a triangular one. The symmetrical stretching frequencies of both were evaluated from Jones' (172) measurements of the reaction rates of Cl_2 with H_2 and HT at 0°C. Using these values, appropriate thermodynamic data, and an estimate of the tunnel effect, they calculated the relative reaction rates of Cl_2 with H_2, D_2, HD, and HT as a function of temperature. The results agree with the experimental values but more extensive and precise measurements on the D_2 and HD reactions are necessary to determine which structure is the correct one.

Bunton, Craig & Halevi (173) made a theoretical analysis of isotope fractionation effects in isotopic exchange reactions. They developed the kinetics of two general types of reactions: the exchange of X* between AX_n and BX_m, and the exchange of X* between AX and X. They find that in most practical cases (low isotopic abundance of the labelled atom, small isotope effects, or both) no deviation from first order kinetics should be observed for either reaction. They also present quantitative methods for determining the

deviation in systems in which the isotopic abundance of the labelled atom is large, and large isotope effects are involved.

Weston (174) reported preliminary measurements of the variation in the kinetic isotope effect in the isomerization of cyclopropane. His purpose was to test the Lindemann theory of unimolecular reactions. According to the theory a reactant molecule obtains activation energy by collisions with a second molecule. Thus the reaction rate at high pressures is determined by the decomposition rate of the activated complex and an appreciable isotope effect could be expected. At low pressures, the rate is controlled by the rate of collision which in this case involves a much smaller isotope effect. Weston's experiments with tritium-labelled cyclopropane support the theory. The experiments were conducted at 470–490°C. on the tracer level so that the tagged species was largely C_3H_5T. The observed k'/k values were 1.129 $\pm$0.027 at 700 mm. Hg and 1.004 $\pm$ 0.010 at 0.4 mm. Hg. From these data Weston obtained a k_T/k_H ratio of 0.28. The isotope effect indicates that the critical coordinate is along a C—H rather than a C—C distance.

Friedman, Bernstein & Gunning (175) measured the C^{13} isotope effect in the thermal decomposition of C_2H_5Br to $CH_2=CH_2$ and HBr. Their analysis of the results led them to the conclusion that the reaction proceeds by the unimolecular abstraction of HBr. Shortly thereafter Maccoll & Thomas (176) suggested that the following free radical mechanism was more consistent with the observations:

$$CH_3CH_2Br \rightarrow CH_3CH_2 + Br$$
$$Br + CH_3CH_2Br \rightarrow CH_2CH_2Br + HBr,$$

followed by the chain reaction

$$CH_3CH_2Br \rightarrow CH_2CH_2 + Br$$
$$Br + CH_3CH_2Br \rightarrow \text{end of chain.}$$

Friedman, Bernstein & Gunning (177) subsequently indicated general agreement with the comments of Maccoll & Thomas.

Bernstein (178) measured the fractionation of O^{18} in the reaction of copper with natural O_2 over the range 68–256°C. Analysis of the oxide film indicates that the O_2^{16} reacts preferentially to $O^{16}O^{18}$. The effect appeared to be independent of pressure over the limited range studied (2–25 cm. Hg). The fractionation factor was 2 per cent at 150°C., and the activation energy was 17 cal./mole. He concluded that the mechanism of the fractionation involves an isotopic exchange equilibrium between gaseous O_2 and chemisorbed oxygen atoms and that the isotopic composition of the oxide is the same as that of the adsorbed layer.

Gelles & Reed (179) measured the C^{13} isotope effect in the decomposition of oxaloacetic acid in aqueous solution under the following conditions: alone, in the presence of diamagnetic Y^{+++}, and in the presence of paramagnetic Dy^{+++}. The observed ratios of the rates of C^{12}—C^{12} to C^{12}—C^{13} rupture are 1.06, 1.05, and 1.10 respectively. The authors point out that the C^{13} nuclear

spin-electron spin interaction is comparable to the electron spin—electron spin interactions produced by the Dy^{3+}; they suggest that this could account for lower relative effect of the paramagnetic ion on the rate of C^{12}—C^{13} rupture. Since C^{14} has zero spin, no magnetic effect on the relative rate of C^{12}—C^{14} to C^{12}—C^{12} rupture is expected. The authors plan to confirm this point.

In 1954, Stevens & Crowder (180) reported a reverse isotope effect of 7 per cent in the condensation of o-benzoylbenzoic acid-carboxyl C^{14} to anthraquinone. Ropp (181) repeated the experiment and observed a normal isotope effect of 3.5 per cent, in agreement with theoretical predictions based on an approximate model. He suggests that the apparent reverse effect in the earlier work really arose from an isotope dilution which followed the synthesis of the acid. He is continuing work on this problem in a joint effort with the original investigators.

Yankwich & Weber (194) investigated the intermolecular isotope effect of C^{12} and C^{13} on the decarboxylation of the mono-anion of malonic acid in quinoline solution over the temperature range 67.5–119°C. Their measured values for the rate constant ratios appear to be in slight disagreement with values calculated on the basis of the Bigeleisen model. The authors believe that such disagreement could be due to anion-solvent equilibria preceding the bond rupture process. Yankwich & Belford (195) previously advanced this suggestion to account for the apparent discrepancy between theory and experiment for the intermolecular carbon isotope effect on the decarboxylation rate of undissociated malonic acid.

Stranks (182) studied the photochemical exchange reaction

$$C^{14}O + COCl_2 \rightleftharpoons CO + C^{14}OCl_2$$

The rate data are consistent with an exchange mechanism involving the two reactions

$$COCl \rightleftharpoons CO + Cl$$
$$COCl + Cl_2 \rightarrow COCl_2 + Cl$$

The isotope effect on the equilibrium constant of the over-all reaction (147) arises from the multiplication of the undirectional step by the effect of the free radical equilibrium. The observed quantum yield for the primary dissociation of $COCl_2$ by 2537 A. light is unity for both the C^{12} and C^{14} species.

Stranks (183) also studied the rate of thermal exchange between $C^{14}O$ and $COCl_2$ in the presence of equilibrium quantities of Cl_2 at 375–450°C. Assuming the mechanism of Bodenstein and Plaut, and correcting for the isotope effect (ranging from 0.5–1.5 per cent) he obtained the rate equation for the thermal decomposition of $COCl_2$ to CO and Cl_2. The results are in agreement with the older data of Bodenstein.

Kaplan (184) measured the tritium isotope effect in the oxidation of propanol-2 to acetone by chromic acid. His results on $(CH_3)_2CTOH$ are consistent with earlier work on the deuterium species. The presence of Mn^{++}

inhibits the oxidation of propanol by the lower valent states of chromium. In the absence of Mn^{++}, k_T/k_H went from 0.13 in 0.3M $HClO_4$ to 0.26 in 2M acid. He concluded that the C—H rupture, which occurs in the rate-determining step of attack by Cr^{VI}, must predominate in the slow steps of the subsequent oxidation by the lower valent species. Attack at the hydroxyl H may occur at high acid concentrations.

Kaplan & Wilzbach (185) examined the effect of isotopic substitution on the rates of hydrolysis of triphenyl and tripropyl silanes in piperidine-H_2O and C_2H_5OH—H_2O solutions. Substitution of D or T in either the silane or the solvent reduced the rate. Thus the Si—H bond rupture controls the rate. Also it appears that in the transition state the hydrogen atom from the silane is bonded to that of the solvent.

Wiberg & Stewart (186) measured the rate of oxidation of aromatic aldehydes to acids by permanganate in the pH range 5–13. The compounds with deuterated aldehyde groups were oxidized considerably slower than the corresponding protium compounds in neutral solution, but the isotope effect decreased with increasing pH. Tracer experiments with O^{18} indicated that in neutral solution, the permanganate is the major source of the oxygen introduced to the aldehyde, whereas at high pH solvent water is the source. They conclude that the reaction in neutral solution involves formation of a permanganate ester of the hydrate of the aldehyde; this is followed by the rate determining step, a loss of the aldehyde hydrogen. The mechanism of the base-catalyzed reaction is not clear; a free radical chain mechanism may be involved.

Swain, Cardinaud & Ketley (187) found that the hydrolysis of t-butyl chloride is 40 per cent faster in H_2O than in D_2O, whereas the t-butyldimethyl-sulfonium ion and methyl halides have the same solvolysis rates in both solvents. The reaction rate of methyl halides with pyridine is also unaffected by the substitution of D_2O for H_2O as the solvent. Since t-butyl chloride is more dependent than the others upon electrophilic solvation in the rate determining step, the results indicate that H_2O is a better electrophilic reagent than D_2O.

McNesby & Gordon (188) studied the photolysis and pyrolysis of $(CD_3)_2CO$ in the presence of C_2H_6, and of $(CH_3)_2CO$ in the presence of C_2D_6. For the reactions:

$$CD_3 + C_2H_6 \rightarrow CD_3H + C_2H_5$$

and

$$CH_3 + C_2D_6 \rightarrow CH_3D + C_2D_5,$$

they obtained activation energies of 11.5 and 14.8 kcal./mole respectively.

A review paper by Wiberg (169) provides a comprehensive summary of deuterium isotope effects in reaction kinetics.

Isotope Effects in Mass Spectra

Little activity was reported in this field in 1955; only two papers were found (189, 190). Consequently good experimental data are still sparse and it is still too early to make an accurate evaluation of the proposed theoretical models.

Schaeffer & Owen (189) measured the relative changes in the probability of bond rupture following electron impact for isotopic molecules of O_2 and CO_2. They found that the ratio of bond breaking in $O^{16}O^{18}$ to that in O_2^{16} is 0.98. They also found the relative yields of isotopic forms of C^+, CO^+, and O^+ from $C^{12}O^{16}$, $C^{13}O_2^{16}$, and $O^{16}C^{12}O^{18}$. Their CO^+ data from $C^{12}O_2^{16}$ and $C^{13}O_2^{16}$ do not agree with values previously published; they get a $C^{13}O^{16+}/C^{12}O^{16+}$ value of 0.974 ± 0.004 which compares with the 0.948 obtained by two other laboratories. Their C^{13+}/C^{12+} value for these two molecules is 1.022 ± 0.006 which agrees with Stein's earlier value (191) but is in conflict with the 0.961 of Dibeler *et al.* (192).

Schaeffer (190) calculated the relative changes in pattern for O^{18} and C^{13} substituted CO_2 using the Franck-Condon mechanism for bond rupture. The agreement between the observed and calculated yields, although adequate, could be better. However, there is excellent agreement between calculation and experiment as to which bonds break more easily. Apparently the electron impact process for the simpler molecules is satisfactorily described by the Franck-Condon mechanism. Schaeffer points out that this does not mean that the more complicated molecules will necessarily behave in this manner. For these, the statistical model (193) may apply.

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MAGNETIC RESONANCE[1]

By Clyde A. Hutchison, Jr.

Enrico Fermi Institute for Nuclear Studies and Department of Chemistry, University of Chicago, Chicago, Illinois

Introduction.—The elementary theory of magnetic resonance phenomena has been presented in previous reviews of this series by Gutowsky (1) and by Shoolery & Weaver (2). The basic principles underlying both nuclear and electronic magnetic resonance have been described in these reviews and in addition the chief applications to chemical problems have been outlined. The present review therefore proceeds immediately to a summarization of the literature which has appeared on these subjects during 1955 (January 1955 through December 1955). Familiarity with these previous reviews is assumed. The literature of magnetic resonance in atomic beams is not considered here. Also space does not permit a review of the work on certain subjects in the field of electronic magnetic resonance, namely, ferromagnetic resonance, ferrimagnetic resonance and antiferromagnetic resonance on each of which a considerable amount of work has been published during 1955. No mention is made below of certain types of resonance phenomena related to those discussed here which are observed in condensed phases but which are electric and not magnetic resonances, although magnetic fields are frequently employed in their study, namely, pure quadrupole resonance, cyclotron resonance and plasma resonance.

General Reviews.—During the year several general reviews of magnetic resonance phenomena have appeared. The book by Ingram (3) reviews both nuclear and electronic resonance and discusses many applications to chemical problems. The review by Wertz (4) also covers the literature on both subjects and discusses 627 articles which have appeared. The book edited by Braude & Nachod (5) contains a chapter by Hutchison which discusses applications to organic chemical structural problems. Bowers & Owen (6) have given a very complete and detailed review of all the work which has been published on electronic resonance in crystalline substances with particular reference to the application of the crystal field theory in single crystal studies.

General Theory.—A number of contributions to the general theory of electronic and nuclear magnetic resonance have appeared. Pines & Slichter (7) have discussed a simplified model in terms of which one may arrive at results, in connection with a variety of magnetic resonance problems, which are in agreement with those of very detailed theories. This model is based on a consideration of spin dephasing as a random walk problem. In terms of this model the physical basis for the effect of motion in narrowing resonance lines is clearly evident and in many problems, a number of examples

[1] The survey of the literature pertaining to this review was completed in December, 1955.

of which are given, answers may be obtained simply and conveniently. Kaplan (8, 9) has given a method of derivation of resonance equations applicable to systems with a single relaxation time. Considerable interest has been expressed in the theory of magnetic resonance for arbitrary field strengths, particularly in low magnetic fields. Garstens & Kaplan (10), Bene & Extermann (11) and Wangsness (12) have all made contributions to this problem. The Bloch equations require modification in order to account for the low field results, particularly the existence of finite absorption at zero field in the case of purely spin resonance. The general theory of the effect of temperature on line shape has been given by Gross (13). The problem of the nuclear hyperfine structure in electronic resonance absorption has been reconsidered by Abragam *et al.* (14). They have shown that unpaired s-electrons play an important part in hyperfine structure even when the nominal electronic configuration for an atom or ion has no unpaired s-electrons. In the 3d transition group the central density of unpaired electron spins is nearly the same in all ions of the group. For neutral atoms it is more variable but of the same magnitude. These authors attempted an *a priori* calculation of the magnitudes of the hyperfine splittings. The interactions which they calculate have the correct sign but are about 10 times too small. The full explanation of the s-electron effects on nuclear hyperfine interactions in the transition elements is still an open question. Eisenstein & Pryce (15) have developed the theory of bonding in uranyl type ions and have shown that both the magnetic susceptibility and the electronic resonance results required that the unpaired magnetic electrons in the molecule-ions NpO_2^{++} and PuO_2^{++} are f-electrons. They have also shown that f-electrons play an important role in the chemical bonding in these molecules.

Herzfeld (16) has made calculations of energy states and g-values for electronic resonance in transition elements in which the crystal field perturbation breaks down the Russell-Saunders coupling of the free ion. The applications of the results to the cases of chromium alums and fluoride and to some molybdenum fluorides are discussed.

Judd (17, 18) has extended the theory of the crystal field perturbations of rare earth ions to include the excited states and the case of C_{3v} symmetry. He has discussed in particular the rare earth double nitrates, $X_2Y_3(NO_3)_{12} \cdot 24H_2O$, in which X is a rare earth and Y a divalent ion. The values of the various parameters of the theory have been evaluated and found to vary in a systematic fashion throughout the rare earth series.

Electronic Magnetic Resonance

Single Crystals.—The experimental evaluations of the parameters in the spin Hamiltonian for electronic resonance in single crystals of compounds of rare earth and transition group elements have been continued and extended, for the most part by the Oxford group of workers (19 to 28). Considerable extension of the theory of the crystalline field perturbations and the nuclear hyperfine interaction has been made by the same group. Bleaney *et al.*

have studied terbium (III) in the yttrium ethylsulfate structure (19), cesium titanium alum (20), holmium (III) in yttrium ethylsulfate (21), praseodymium (III) in yttrium ethylsulfate (22), copper (II) in copper Tutton salts diluted with isomorphous zinc salts (23, 24, 25). Cooke & Duffus (26) have investigated the magnesium double nitrates with praseodymium, neodymium and samarium. Nuclear spins of ^{147}Sm, ^{149}Sm, ^{165}Ho, and ^{159}Tb have been determined from the hyperfine patterns. Bleaney & Low (27) have determined the nuclear spins of ^{151}Eu and ^{153}Eu from hyperfine structure in powdered strontium sulfide phosphor containing divalent europium. Nuclear magnetic moments have been estimated from the magnitudes of the hyperfine splittings in the cases of ^{151}Eu, ^{153}Eu, ^{159}Tb, ^{165}Ho, and ^{141}Pr. The largest error in these cases, by far, in the determination of nuclear magnetic moments from the magnitude of the splittings is in the value assumed for the mean value of r^{-3} (r is the distance from the electron to the nucleus). A method of arriving at values of this quantity in the case of rare earth ions has been discussed by Bleaney (28). Nuclear electric quadrupole moments have been estimated from quadruple effects on the hyperfine structure pattern in the cases of ^{165}Ho, ^{63}Cu, and ^{65}Cu (See Table I). The cases of holmium and praseodymium are examples of situations in which small deviations from the nominal symmetry of the crystalline field arising from Jahn-Teller effect and crystal strains permit observation of a resonance when the rf field is parallel to the static field and give rise to the characteristic asymmetrical line shapes assumed to be due to a Gaussian distribution of the magnitudes of such deviations. These effects and other interesting features of the crystal field perturbations are discussed in the references mentioned above.

TABLE I

NUMERICAL VALUES OF NUCLEAR PROPERTIES AS MEASURED BY MAGNETIC RESONANCE METHODS

Isotope	Nuclear Spin	Magnetic Moment Nuclear Magnetron	Nuclear Electric Quadrupole Moment cm^2
^{151}Eu	5/2	Ratio 151/153	—
^{153}Eu	5/2	2.23 ± 0.03	—
^{147}Sm	7/2	—	—
^{149}Sm	7/2	—	—
^{165}Ho	7/2	3.29 ± 0.17	$+2 \times 10^{-24}$
^{159}Tb	3/2	1.5 ± 0.4	—
^{141}Pr	5/2	3.9 ± 0.2	—
^{63}Cu	—	Ratio 65/63	Ratio 63/65
^{65}Cu	—	1.069 ± 0.003	1.08 ± 0.02

In addition Singer (29) has studied single crystals of trichelates of chromium and Singer & Kikuchi (30) have investigated single crystals of the organic free radical α,α'-diphenyl-β-picrylhydrazyl. Hutchison & Anderson (31) have reported results on praseodymium in lanthanum trichloride structure which later proved to have their origin in a neodymium impurity. Tinkham (32, 33) has studied divalent ions of manganese, cobalt and iron in the zinc fluoride structure. Divalent manganese has been examined in a number of environments; in zinc sulfide by Matarrese & Kikuchi (34), in calcite by Kikuchi (35), in sodium chloride by Oshima *et al.* (36) and in zinc sulfide by Muller (37). One interesting result of Tinkham's studies is the importance of covalent bonding and charge transfer to the neighboring anions, even in such an ionic crystal as this, which must be assumed to account for the experimental results. In fact the interaction with the neighboring fluorides results in a superhyperfine interaction leading to a corresponding structure of the resonance line. Coupling constants for this structure as large as 10–20 gauss are observed. In the case of trivalent chromium in the same crystal the superhyperfine structure is not observed, presumably because it has no magnetic electrons in σ-bonding orbitals and hence cannot attach the s-functions needed for the large interactions with the fluorine nuclei. Owen (38) has shown that optical and magnetic data are reconciled if covalent bonding is assumed in octahedrally coordinated (with water) complexes of 3d, 4d and 5d ions. The orbital contributions to the magnetic moments are smaller than would be expected on the basis of a purely ionic model. The bonding also gives reduced term separations and reduces the hyperfine splitting from the central nucleus. It also affects the exchange interaction between neighboring metal ions.

Bennett & Ingram (39) have studied electronic magnetic resonance in single crystals of copper phthalocyanine and interpreted the results in terms of the crystal field theory and the known structure. Bennett *et al.* (40) have examined resonance in ferrihemoglobin and hemin. Instead of the expected $g = 2.00$ the magnetic susceptibility having indicated ionic bonds, they found a g equal to about 6 in the plane of the heme and along an axis normal to this plane about 2.5. Moreover the azide and cyanide complexes of ferrihemoglobin previously called essentially covalent on the basis of susceptibility measurements were found to have g's quite different from the inorganic complex ferricyanide ion. Similar results were observed for ferrimyoglobin.

Free Radicals.—The semiquinone ions have been the most frequently investigated free radicals throughout the year. Venkataraman & Fraenkel (41) have reported on the semiquinones formed by the oxidation of hydroquinones or the reduction of quinones in alkaline media. In the case of the oxidation of hydroquinone a strong resonance is observed with a structure consisting of five peaks in the intensity ratios 1:4:6:4:1. If the radical observed were the negative ion of the semiquinone of p-benzoquinone there would be four equivalent protons producing hyperfine structure giving the

observed results. When p-benzoquinone was oxidized, the same hyperfine pattern was observed, and a considerable number of additional lines which change in intensity, as the reaction proceeds, at a different rate than does the five line pattern. In the case of tetramethyl-p-benzoquinone the pattern consists of thirteen equally spaced lines. Twelve methyl groups with protons all equivalently influencing the magnetic electron would give such a spectrum. They also found resonances in reduced 9,10-phenanthrenequinone and p-toluhydroquinone and in a mixture of benzil, benzoin and alkali. The resonance had very complex hyperfine structures. Venkataraman & Fraenkel (42) extended their results to semiquinone ions of 2,5-dimethyl-p-benzoquinone and 2,6-dimethyl-p-benzoquinone. Blois (43) has reported resonance in semiquinones of o- and p-benzoquinone; Hoskins (44) in the semiquinones of substituted o-benzoquinones; Wertz & Vivo (45) in the semiquinone ions of benzoquinone, chloroquinone, 2,3-dichloroquinone, trichloroquinone, and tetrachloroquinone. No chlorine splitting is observed. In the case of phenylbenzosemiquinone ion (45) no effect of the phenyl group shows up in the hyperfine structure. These results give insight into the distribution of the odd electron over the molecules. Semiquinone-type radicals were found in the one electron reduction of nitrogen compounds such as riboflavin, Hoskins & Loy (46) identified the hyperfine structure patterns of the resonances found in oxidized pyrogallol as arising from semiquinone-type structures. The explanation of the occurrence of such pronounced splittings (separations between components up to several gauss are observed) is not obvious. The π-electron wave functions have a node in the plane of the ring in which the protons producing the structure lie, and it is therefore difficult to see how an interaction of this magnitude occurs. Venkataraman & Fraenkel (41) calculate the separation to be expected on the basis of the mechanism proposed by Weissman in which out-of-plane proton vibrations produce the interaction and find the resultant splittings to be an order of magnitude smaller than those observed. These authors suggest hyperconjugation effects as a possible cause of the large interaction. McConnell (47) has suggested that indirect couplings of nuclear spins with electron spins by way of valence electrons may account for the size of the observed splittings.

Bamford *et al.* (48) have used magnetic resonance methods to detect the chain propagating free radicals produced in the polymerization of acrylonitride which are trapped in or occluded by the polymer as it forms thereby resulting in the characteristic rate laws governing the reaction. Wertz *et al.* (49) have described the resonances in pentaphenyl cyclopentadienyl, α,γ-bis-diphenylene-β-phenylallyl, tri-t-butyl phenoxyl and 2,6 di-t-butyl-4-phenyl phenoxyl. Wertz & Vivo (50) have observed free radicals arising from p-thiocresol and thiophenol in sulfuric acid. They have discussed the interpretation of the observed hyperfine structure. Gilliam, Walter and Cohen have studied the resonances in the triarylamminium perchlorates. Hyperfine structures result from the nuclear moment of the nitrogen atoms, and it can be deduced that the three bonds to the nitrogen form a pyramidal

structure. Bennett *et al.* (52) found resonance in sodium and potassium superoxides at 90°K. attributable to the ion, O_2^-. The theory of the resonance is discussed and predicted g-values in good agreement with those observed are obtained. They also studied potassium ozonate and frozen solutions of chlorine dioxide. Hyperfine structure from the chlorines was resolved in this last case.

Irradiated Materials and Color Centers.—Electronic magnetic resonance methods continue to serve as important tools for studying the effects of radiation of various types on matter. O'Brien (54) has studied the color centers produced in quartz by irradiation with x-rays. The nuclear hyperfine structure of the magnetic resonance absorption shows that each color center so produced is associated with an aluminum atom which exists as an impurity in the quartz. The proposed model which accounts for the observations on hyperfine structure puts this aluminum atom at a silicon site in the quartz structure and the unpaired electron on one of the nearest oxygen atoms. The symmetry of the g-tensor is also accounted for by this model and the optical properties may be successfully interpreted in terms of it and certain numerical quantities measured by the magnetic resonance experiment. Matheson & Smaller (55) have studied the magnetic resonance in paramagnetic species produced by the γ-irradiation of ice and deuterated ice at 77°K. They identified the magnetic absorbers produced by ^{60}Co irradiation, by means of the nuclear hyperfine structure as H and OH (or D and OD). The ratio of the splittings in the H doublet and the D triplet was $4.0 \pm .4$ in agreement with the atomic beam value 4.3. However the magnitude of the splitting is much less than for the free atoms (e.g. a splitting constant of 55.5 mc. sec.$^{-1}$ for H compared with 1420 mc. sec.$^{-1}$ for H in the 1s state). It is believed that the strong intermolecular electric dipole field may account for this deviation. When the solid H_2O is cooled to 4°K. a second doublet appears with a separation of 10 gauss instead of the 30 gauss observed at 77°K., and signs of a second triplet occur in D_2O. These new peaks are interpreted as arising from OH and OD, and this is confirmed by studies of irradiated H_2O_2 in H_2O and D_2O_2 in D_2O. The yields of free radical species in the irradiation may be determined, and the results are of considerable importance to the study of the radiation chemistry of aqueous systems. The same workers have also studied irradiated ammonia and formic acid.

Portis (56) and Portis & Shaltiel (57) have extended the investigation of F-centers in alkali halides. Relaxation effects and line shapes and widths have been interpreted in terms of the rapid passage theory of Bloch; in particular they have explained the observation that the absorption signal of the color centers lags the magnetizing field by $\pi/2$. Kanzig (58) has observed a large resolvable hyperfine structure due to v-centers in alkali halides. From analysis of the structure he concludes that the electron hole is localized on two negative ions only i.e. the v_1-center is essentially a Cl_2^- molecule-ion, presumably near a positive ion vacancy. The g-shifts and the

splittings are explained quantitatively by axially symmetric Cl_2^- along 110 axes. The variation of splitting with angle of crystal with respect to the magnetic field permits the determination of the relative amounts of s and p character of the wave functions involved. Ard (59) has observed resonance in color centers produced by x-irradiation of $NaNO_3$, and has discussed the interpretation of the results showing that one set of lines results from interactions of the color centers with nitrogen atoms. Schneider (60) and Ard *et al.* (61) have studied the resonances in x-rayed Teflon (polytetrafluoroethylene). Schneider found a barely resolved triplet with a separation of 19 gauss believed to be due to an interaction of unpaired electrons with fluorine nuclei, the electrons coming from broken carbon-carbon bonds. These electrons if localized at the breaks would be most influenced by the two adjacent fluorines thus producing the triplet. These results would indicate that this electron plays a part in the carbon-fluorine bonding. The other group of workers finds a symmetrical pattern of eight peaks with an extra peak superimposed near the center if the sample is exposed to air, which does not fit the symmetrical pattern. When the x-rayed Teflon is aged in air this superimposed peak grows at the expense of diminution of intensity of the other, and after two weeks only this one peak remains. If the sample is aged in vacuum or in nitrogen the eight peak pattern does not change. It is believed that the superimposed central peak is due to oxygen absorbed in the holes formed by broken bands plus chain contraction. It is also supposed that the odd electron moves over seven equivalent fluorine atoms and that increased absorption of oxygen puts an end to this migration of the electron by forming a bond with the radicals. Ard & Gordy (62) have found magnetic resonance in hydrogen sulfide and hydrazine chloride irradiated with x-rays at 77°K. They have also studied hydrazine and hydrogen selenide under similar conditions. The resolved hyperfine structure is interpreted in terms of postulated free radicals. Wertz & Vivo (63) have observed resonance due to defect centers in MgO.

Metals and Semiconductors.—Feher & Kip (64) have examined electron-spin resonance in lithium, sodium, potassium, beryllium, magnesium, aluminum, palladium and tungsten. They found no resonances in the last four metals. Their experiments were carried out at 300 and 90,000 mc. sec.$^{-1}$ and from 4 to 296°K. Dyson's theory (65) on shapes was checked, and agreement with the theory was found in both the normal and the anomalous skin effect region. They also found agreement with Elliott's theory of relaxation times in metals arising from spin-orbit coupling. Levy (66) has studied resonance in liquid alkali metals at 300 mc. sec.$^{-1}$ and from 20 to 140°C. There is a linear temperature dependence of line width up to the melting point and then it increases by 25% in a 5°C. range remaining constant at 16.5 gauss up to 140°C. The Elliott theory for spin-lattice relaxation gives a result in agreement with this behavior. Feher & Levy (69) have studied resonance in frozen alkali metal-ammonia solutions and have shown that the resonance arises from particles of the metal. The theory of Dyson (65)

of the magnetic resonance absorption by conduction electrons predicts among other things that diffusion in and out of the skin has no marked effect on the width of the resonance (it might have been supposed that this effect would result in a broadening of the line due to loss of phase coherence), but has a radical effect on the shape resulting in some unusual and characteristic shapes in particular cases. Argyres and Kahn have calculated the g-factor by Yafet's method for metallic Li getting a result in reasonably good agreement with the experiments.

Owen *et al.* (68) have studied electronic resonance in copper-manganese and silver-manganese alloys. The position, width and shape of the resonances depend on composition and temperature. At 0.05 per cent manganese $g \sim 2.0$ at all temperatures. When the manganese concentration is increased g becomes greater than 2 by an amount which varies roughly as the ratio of the concentration to the temperature. No hyperfine structure is observed although the line width is less than the expected hyperfine splitting. The observed resonance is probably due to manganous ions coupled by exchange interactions.

Feher *et al.* (70) have studied the electron spin resonance of impurity atoms in silicon and have observed weak satellites halfway between pairs of the $2I+1$ (I is the nuclear spin) main lines arising from the hyperfine structure due to the magnetic moments of the donor atoms. Slichter (71) suggested that these satellites arose from coupled pairs of electron spins of donor atoms acting as a unit and responding to the average magnetic field produced by hyperfine coupling to the two nuclei involved. The experiments of Feher *et al.* (70) have confirmed this explanation and have revealed other satellites resulting from the coupling of groups of 3 and 4 electrons on donor atoms. Kohn (72) and Kohn & Luttinger (73) have developed a theory of the hyperfine splitting of donor states in silicon which is in good agreement with the spin resonance experiments of Fletcher *et al.* Lark-Horovitz *et al.* (74) have studied spin resonance in neutron-irradiated p-type boron doped silicon and have discussed the resonance due to the defects produced by the irradiation.

Carbon.—Castle (75) has observed magnetic resonance in raw cokes which has a maximum intensity when the material has been heated to near 550°C. and drops rapidly as volatile matter is driven off by further heating. He believes the magnetic absorption arises from nitrogen or oxygen atoms bonded into the coke structure. Although usually the resonance occurs at $g = 2.0030 \pm 0.0002$ some cokes have a strong resonance at $g \sim 6$. Bennett *et al.* (76) have found that this same electronic magnetic resonance may be obtained by charring any natural or artificial carbohydrate and the observed resonance is the same as that found in coal. The resonance also appears in charred diamagnetic organic salts (small variation in line width and g is found to result from the effects of the diamagnetic metal atoms), deposits from luminous flames, charred anthracene, glycerine, vegetable root and other complex organic material, charcoals furnaced below 600°C.,

coals and coal derivatives formed below 600°C. The free radical concentration rises sharply with charring temperature to a maximum at 500°C. and then falls sharply to zero as the charring temperature is raised. They find about one free radical per 2000 carbon atoms. The signal intensity increases linearly with per cent aromatic carbon. They believe that the resonance arises from broken bonds in condensed carbon rings. At 600°C. the volatile matter is removed, and the rings are mobile enough to join up the broken bonds and begin forming graphitic planes. The electrical conductivity begins to rise sharply at this point. This is a quite different resonance from that of the conduction electrons in carbons and graphites reported by others. Castle (77) has observed free electron spin resonance in thermal carbon blacks which he attributes to conduction carriers.

Gases.—The theory of the hyperfine structure of the NO molecule has been developed by Lin & Mizushima (78) and by Dousmanis (79). The resonance absorption in atomic phosphorus has been investigated by Dehmelt (80, 81). A doublet is found which is symmetrical about the free electron g-value with splitting of 20.0 ± 0.5 gauss due to the hyperfine interaction with the P^{31} nucleus. One per cent mixing of the configuration $3s\ 3p^3 4s\ {}^4S_{3/2}$ to the ground state $3s^2\ 3p^3\ {}^4S_{3/2}$ would give these results. Tinkham & Strandberg (82) have interpreted the magnetic resonance spectrum of oxygen gas in terms of their previously reported theory. They discuss the effects of collisions and the dependence of width on M and K.

Miscellaneous Systems.—Pake & Sands (83) have studied magnetic resonance hyperfine structure in aqueous solutions of vanadium ions in various valence states. Gensis & Williams (84) have examined the hyperfine structure of aqueous solutions of manganous salts. Low (85) has observed the hyperfine structure of europium and samarium in strontium sulfide phosphors and confirmed the existence of divalent europium in these phosphors. Smaller *et al.* (86) have observed a resonance in compounds of graphite with lithium, sodium, potassium, calcium and barium. Pastor & Turkevich (87) have studied the resonance in potassium complexes of aromatic compounds. They have studied the solid products of reactions between potassium dissolved in dioxane and naphthalene, anthracene, phenanthrene, pyrene, chrysene, diphenyl, p-terphenyl, p-quatriphenyl, 1,3,5-triphenylbenzene and benzophenone. $g = 2.002 \pm 0.001$ for all of them. There is a linear relationship between the width of the resonance and the chemical resonance energy of the parent organic compound. Ling *et al.* (88) have studied the resonance in powdered chromic chloride. Wertz *et al.* (89) have observed resonance due to impurities in MgO. They found a manganous ion hyperfine structure spectrum each main line having four satellites and another impurity resonance. Gardner & Fraenkel (90) found resonance in ultramarines and suspect that both the blue color and the magnetic resonance are due to a sulfur component on the basis of a comparison with the resonances which they observed in liquid sulfur and in solutions of sulfur. Sands (91, 92) has observed paramagnetic resonance absorptions in a variety of glass samples

with g = 4 and 6. It was assumed that these were anisotropic g-values for a specific impurity and the recorded peaks resulted from a distribution of Stark fields over all directions. Resonances were also found with g = 2. These last showed nuclear hyperfine structure characteristic of known paramagnetic impurities.

Becker (183) has studied resonance in α,α'-diphenyl-β-picrylhydrazyl and in Wurster's Blue at very low fields. He finds that the maximum in the absorption curve disappears at 1.3 mc. sec.$^{-1}$.

Apparatus and Techniques.—Hirshon & Fraenkel (93) have described a high-sensitivity automatic recording electronic magnetic resonance absorption spectrometer operating at a wavelength of 3.2 cm. Burgess & Norberg (94) have applied a double resonance technique to the free radical peroxylamine disulfonate ion. They applied an intense rf radiation field near one of the hyperfine structure component frequencies and detected resonance absorption at a second transition employing a low rf level. There should be a broadening and enhancement of the detected line as the first transition becomes saturated because of population distribution effects and interactions, but in certain cases a bump is observed to appear on the absorption curve. It is shown that the position of this bump depends on both the intensity of the saturating field and the values of the two applied frequencies. The condition for getting the bump is that $\nu_s+\nu_d=\nu_{ab}+\nu_{bc}=\nu_{ac}$ where ν_s, the saturating frequency, is near resonance with the transition frequency, ν_{bc}; and ν_d, the detecting frequency is near resonance with the transition frequency, ν_{ab}. With ν_s and ν_d fixed an increase in the amplitude of the saturating field increases the shift of the bump and of the detected transition.

Nuclear Magnetic Resonance

Single Crystals.—Eades (95, 96) has investigated the resonance of ^{27}Al in euclase ($HBeAlSiO_5$). It is found that the aluminum nuclei occupy two types of lattice sites which differ only in orientation of the principal axes of the electric field gradient tensors, whose eigenvalues are all distinct but identical at both sites. The values of quadrupole coupling constant and asymmetry parameter are determined. The results on the structure are consistent with the x-ray determinations of the structure. Waterman & Volkoff (97) have examined the resonance of ^{11}B in kernite ($Na_2B_4O_7\cdot 4H_2O$). They find four non-equivalent B sites and determine the orientation of the four electric field gradient tensors. The quadrupole coupling constants and the asymmetry parameter are determined. The structure results on the boron are consistent with the structure as determined by x-rays but preliminary results on ^{23}Na in the same crystal gives results in disagreement with the x-ray results. Spence (98) has made measurements on the proton resonance in barium chlorate monohydrate. He finds that the unit cell contains six water molecules with the lines of proton pairs all pointing along the same direction parallel to a (010) plane. He measures the proton-proton

distance and angle and finds that they compare well with the crystal structures determined by other methods. Pendred & Richards (99) have studied proton and fluorine resonances in rubidium and ammonium fluoborates at 20°K. and 90°K. They determine the boron-fluorine distance. In the ammonium salt the proton line is narrowed by molecular motion even at 20°K. It is assumed that there is a hindered motion of the ammonium ion about a C_2 axis with a very low potential barrier. It is also determined that in ammonium fluoborate there is only weak hydrogen bonding. Segleken & Torrey (100) have studied the resonances of ^{27}Al in the alums $AlK(SO_4)_2 \cdot 12H_2O$ and $AlNH_4(SO_4)_2 \cdot 12H_2O$. They find a splitting by quadrupole interaction with small trigonal fields along the body diagonals of the unit cube cell of the structure.

Shulman *et al.* (101) have shown that the nuclear resonances in indium antimonide and gallium antimonide show no quadrupole splittings which indicates a very high degree of crystal perfection. However, they found that by stressing crystals of these substances they could produce quadrupole broadening of the nuclear magnetic resonance lines because of the distortion which creates electric field gradients at the nucleus in question. In indium antimonide a stress of 500 lb. in^{-2} along the 110 axis reduced the intensity of the ^{115}In resonance by 11 per cent and increased the second moment of the line by 30 per cent. eqQ is about 45Kc. $sec.^{-1}$ under these conditions.

Widths and Moments.—Powles & Gutowsky (102) have discussed the theory of the reorientation mechanism in the rotational motion of methyl groups in solids. These motions of course have important effects on the widths of the proton magnetic resonance lines. They have discussed two classical models for such reorientation; Brownian type rotation by random angles and random jumping between fixed positions $2\pi/3$ apart. They have also considered a third model involving quantum-mechanical tunneling. As far as predictions of second moments of the absorption lines as a function of temperature the two classical models are the same but the quantum-mechanical model results are different. Data for methyl chloroform, 2,2-dinitropropane and 2-chloro-2-nitropropane can be fit to either the classical models or the tunneling model by suitable adjustment of the potential barriers. However activation energies for classical rotation are low, $\sim$2.2 kcal. $mole^{-1}$ and the observed frequency factors of 10^7 are unexplained. Tunneling requires larger barriers, $\sim$5 kcal. $mole^{-1}$ and the predicted frequency factors agree well with experiment. In 2,2-dichloropropane a classical motion is indicated by a large frequency factor, 10^{12}.

A number of investigations of resonances in rubbers, polyamides and other polymers have been made in which width and second moment changes with temperature have been correlated with structural changes. Banas *et al.* (103) have studied proton resonance in unvulcanized natural rubber, butyl rubber and Paracril 35 from liquid nitrogen to room temperature. They find two abrupt changes of width with temperature. One is attributed to a rotational motion of parts of the molecular chains and the other to a

second-order phase transition of the polymers. Banas & Mrowca (104) have extended these observations to polymethyl methacrylate, polyisobutylene and silicone rubber. Odajima *et al.* (105) have studied the glassy to rubbery transition in polymers by means of proton resonance and discuss the hindered motion of the main chains and side chains in terms of observed line width transitions. Phillips (106) has examined the restricted rotation about the carbon-nitrogen bond in amides which is important in considerations of protein structure. In N,N-dimethyl formamide he observes two resonances which shows that there is restricted rotation since free rotation would result in only one resonance. It can also be determined that the rotation frequency must be less than 38 cycle sec.$^{-1}$ which corresponds to a rather high potential barrier to the rotation. He has also shown that the existence of single methyl proton resonances in N-methyl formamide and N-methylacetamide indicates that only one of two possible rotational isomers is present. Slichter & Mays (107) have examined proton resonance in polyamides from -195 to $+140$°C. There is a marked decrease in the width of the resonance over a 20–30°C. range somewhere between O and 120°C. This results from the onset of the rotation of chain segments.

Kromhout & Moulton (108) have measured line-widths and second moments of proton resonance in ten amines, amides, and acids. They find that hydrogen bonds strongly affect the structures. They find evidence for the existence of glycine in a dipolar form in the solid state. They have measured nitrogen-hydrogen bond distances in urea and glycine. Widths are correlated with rotation of NH_2 groups, and they find that in urea the hydrogen bonds strongly hinder the rotation of these groups.

Segall & Aston (109) have observed line-width changes in the proton resonance in 2,3-dimethylbutane which can be explained on the basis of the following model. When the compound is cooled below the reversible rotational transition temperature, 136.07°K. the rotating state persists to quite low temperatures. However somewhere in the vicinity of 64°K. the rotation gets locked in by some interaction which produced a state which is not the normal non-rotating state which exists at the reversible transition temperature. Then when the sample is warmed the locked-in state persists until at about 103° K an irreversible transition to the normal nonrotating state takes place accompanied by a marked liberation of thermal energy. Shidei & Yano (110) have used proton resonance to study the hindered rotation of water of hydration in magnesium chloride hexahydrate and magnesium bromide hexahydrate.

Norberg & Holcomb (111) have found that the spin-spin relaxation times of ^{7}Li and ^{23}Na decrease sharply on melting of the metals but that there is no corresponding reduction in the spin-lattice relaxation time. The decrease in the spin-spin time arises from an interaction unaffected by diffusion or from local magnetic fields which have no components effective for spin lattice relaxation.

Reif (112) has employed nuclear resonance as a tool for studying point

defects such as vacancies, interstitials and impurities in ionic crystals. If the nucleus observed has a large quadrupole moment, one may study the line widths due to static second-order quadrupole interaction with defects and also the contribution to the spin-lattice relaxation time of the quadrupole interaction with fluctuating fields caused by diffusing defects. He studied the bromine resonance in silver bromide. The motion of silver vacancies leads to a characteristic minimum in the spin-lattice relaxation time at 0°C. The data show the association of defects in silver bromide below 200°K. In sodium chloride and lithium bromide the results show motional narrowing due to diffusion of defects.

Newman *et al.* (113) have studied proton resonances in coals. The variations in the second moments are attributed to variations in the ratio of the number of protons present in saturated hydrocarbon chains or rings to the number attached to aromatic or graphitic structures, since aromatics have second moments of about 10 gauss^2 and aliphatics about 26 gauss^2. The relative proportion of aliphatic protons increases as the carbon content of the coal decreases. Jain *et al.* (114) have studied proton resonance in the liquid crystals 4-4′ methoxyazoxybenzene, 4-4′ methoxy-D_3-azoxybenzene and 4-4′ ethoxyazoxybenzene. The resonances in the liquid crystal phase have a different structure than in either the liquid or the crystal phases. This structure has been explained on the basis of dipole-dipole interactions between protons. Broersma (115) has studied proton relaxation times in mixtures of hydrocarbons with copper sulfate crystals as a function of the crystal size.

Chemical Shifts.—The shift in the resonance frequency or field arising from the differences in electronic environment in molecules is of great importance in many chemical applications of nuclear resonance. Weaver *et al.* (116) measured and tabulated the chemical shifts of ^{17}O in seventeen compounds. They are easily able to measure the shift in oxygen compounds of normal isotopic abundance. The resonance occurs at the highest field in water, and this substance is taken as standard. Holder & Klein (117) have measured and tabulated the chemical shifts for ^{14}N in twenty different bonding situations in compounds. They propose the nuclear resonance technique as a very convenient analytical method.

Shoolery & Alder (118) have studied the proton resonance of water containing various concentrations of diamagnetic salts and measured the shifts relative to pure water. These shifts are interpreted in terms of the breakdown of the hydrogen-bonded structure of water and the ability of the ions to polarize the water molecules. The concentration dependence of the shifts indicates cation-anion interactions at higher concentrations. In all cases except those of Al^{+++}, Be^{++} and very concentrated solutions of zinc a quite narrow single line is observed which shows that the proton exchange rate between the hydrogen bonded structure and the broken down structure is faster than 10^4 sec.$^{-1}$ and that what is being observed is a weighted average of the shifts of the two types of structures. In aluminum trichloride there is a broadened

line whose width depends on the field strength and indicates an exchange rate of about 10^2 sec.$^{-1}$. In zinc chloride and beryllium chloride the high viscosity of the solutions is responsible for an increased line width. They have assigned and tabulated values of the molar chemical shifts of nineteen different ions based on their linear behavior at low concentrations. In general the situation is as follows: near both anions and cations the electrons are pushed off the water protons giving less shielding. On the other hand the breaking of hydrogen bonds by the ions gives greater shielding of the protons. In uni-univalent electrolytes the ions are large, and they break down the hydrogen bonded structure. In this case this is their chief effect and the polarization is less important. The chemical shift is negative. In the case of multivalent ions the polarization is the predominant effect, and the shift is positive. The smaller the ion and the higher its charge the larger the shift becomes.

Hood *et al.* (119) have examined the resonances of protons and fluorine in solutions of trifluoroacetic acid in water. The effects of electrolytic dissociation are seen below mole fraction 0.5, and the effects of hydration above that concentration of acid in water. The dissociation constant is estimated to be 1.8. There is quite a sudden break in the curve of chemical shift versus mole fraction at 0.5, and this results from the fact that below this point there is dissociation equilibrium and above this point an equilibrium between monomer hydrate and dimer. Bhar & Lindstrom (120) have measured the molecular association in propionic acid using proton resonance. They have also studied acetic acid. Weinberg & Zimmerman (121) have measured the proton shifts in mixtures of ethanol and water. There are almost no changes in the chemical shifts of the OH lines of water and ethanol as water is added to ethanol until 20 per cent of water by weight has been added. Then the two lines coalesce because of rapid exchange of protons. Huggins *et al.* (122) have investigated the concentration and temperature dependence of proton resonance in chloroform when it exists in acetone and in triethylamine solutions. They conclude that there is a specific interaction between chloroform proton and the solvent molecule. A one to one complex explains the data. Hydrogen bonds are indicated.

Corey *et al.* (123) have been able to distinguish between cycloheptatriene and bicycloheptadiene structures by means of proton resonances. They have applied the technique in a number of cases.

Kanda (124) has studied the chemical shifts of chlorine, bromine and iodine in metal halides and has shown that the the second order paramagnetism is the source of the large shifts. Covalent bonds play an important part in this situation, and they estimate the degree of covalency from the magnitude of the shift. Bhar (125) has measured the proton shift in ammonia. He studied the effect of pressure on the chemical shift in this compound. The pressure increased the association of the molecules thereby decreasing the diamagnetic shielding, and the resonance field therefore decreases with increasing pressure.

Baker (53) has investigated the chemical shifts and other fine-structure effects, to be discussed later, in pyridine and seven methyl-pyridines. These resemble nitrobenzene except that the ring nitrogen is a much stronger electron sink than is the nitro group. He has discussed the relation of the observed fine-structure to the molecular structure in these cases and shows that there is a more pronounced alteration of charge density in the o-, m-, and p-positions in these pyridines than in the case of nitrobenzene.

Spin-spin Interactions.—The theory of the indirect interactions of non-equivalent magnetic nuclei in molecules via the second order coupling between the nuclear magnetic moments and the spins of the electrons in chemical bonds has been extended by McConnell (126, 47) and by McConnell *et al.* (127). They have employed antisymmetrized single product type molecular spin-oribital wave functions made up from atomic orbitals centered on nuclei. They have found that valence electrons in high energy molecular orbitals, not inner shell electrons, are primarily responsible for the couplings; that the bond-order of Coulson and Longuet-Higgins plays an important role in certain cases; that bond angles are important in determining coupling constants; and that both positive and negative coupling constants will be found. They have developed a systematic procedure for the analysis of the spin-spin multiplets that are observed in high-resulotion nuclear magnetic resonance spectra of liquids. In some simple molecules the situation is quite complicated; e.g. in 1,1-difluoroethylene there are at least eight signals from both ^{1}H and ^{19}F. In perfluoropropylene there are fifty-two distinct signals. They apply their methods to the first of these cases and show that there are ten allowed transitions for both the protons and the fluorines. There is excellent agreement with their theory of the resulting line structures and the experimental ones. Anderson (128) has extended the theory of indirect exchange coupling of nuclear moments by electrons to the cases of semiconductors and insulators. He assumes virtual excitation to triplet states by the hyperfine interaction. The comparison of his theory with the experimental results for indium antimonide and gallium antimonide is satisfactory.

Gutowsky *et al.* (129) have studied the diminution in the magnitude of the spin-spin coupling through the bonding electrons as the two nuclei occur at positions farther and farther apart in the molecule. They find an attenuation by 1/3 per each additional bond between the nuclei in aliphatic compounds. Fluorobenzene gives different results than do the aliphatic compounds. Coupling with the proton gives two peaks and with the fluorine six peaks as if the couplings between all atoms were equivalent. In di- and tetrafluorobenzene the coupling is independent of location. In 1,3,5-trifluorobenzene each proton and fluorine couples mainly with two nuclei of opposite species. Hence the coupling with the para is small compared with that with the ortho. These results do not agree with the expectations on the basis of π-electron interactions which should parallel the case of substituent effects as far as ortho, meta and para positions are concerned.

σ-electron couplings should of course attenuate rapidly around the ring.

Bloembergen & Rowland (130) have found that the width of the resonances of ^{203}Tl and ^{205}Tl in thallium and thallium oxide greatly exceeds the dipolar width and is a function of the abundance of the other isotope. These results are interpreted in terms of an exchange interaction between nuclear spins which exceeds the normal dipolar interaction. Ramsey's theory of nuclear spin exchange via excited states is extended to solids.

Baker (131) has discussed the spin-spin coupling in substituted benzenes and has related the line structures to the molecular structure in p-fluoro ethylbenzene, p-nitrocumene, nitrobenzene and o-dibromobenzene. Baker has also (53) discussed the cases of pyridine and seven methylpyridines.

Solomon (132) has discussed the nuclear Overhauser effect, i.e., the enhancement of the resonance absorption of one nucleus by means of saturating the nuclear resonance of an unlike nucleus in the same molecules. He has studied this effect experimentally in anhydrous hydrogen fluoride. The experimental results are not consistent with a picture of pure dipole-dipole interaction between protons and fluorines without including the effect of other molecules.

Bloom & Shoolery (133) give a theory of exchange interaction between nuclear spins when one is perturbed by an rf field. Experiments on Na_2PO_3F in aqueous solution confirm their theory. They use transmitters tuned to both the fluorine and the phosphorus resonances and a receiver tuned only to the fluorine signal. The spin-spin doublet separation of the received fluorine signal changes as the phosphorus transmitter frequency is varied. Variation of the power level of the phosphorus transmitter changes the fluorine pattern. Herzog & Hahn (134) have shown that proton magnetic resonance absorption in paradichlorobenzene increases the spin-spin relaxation time of ^{35}Cl from 1.1 millisec. to 5.9 millisec. and narrows the ^{35}Cl static line width. Pure quadrupole resonance of sodium in sodium chlorate and sodium bromate modifies the spin-spin relaxation time for ^{35}Cl and ^{81}Br. In this way the Zeeman splitting and quadrupole interactions of sodium were measured. Proctor & Tanttila (135) observed a decrease in population difference between quadrupole energy levels of ^{35}Cl in sodium chlorate following a long pulse of ultrasonic excitation at the transition frequency. Walsh *et al.* (136) have used two oscillating magnetic fields both perpendicular to the static field to measure spin-lattice relaxation times. The static field is modulated by a square wave so that the nucleus first has a Larmor frequency equal to that of the one oscillator and then that of the other. One of the ac fields is below saturation and the other saturates in a time short compared with the period of the square wave. If power absorbed at the nonsaturating frequency is plotted against the period of the square wave the spin-lattice relaxation time may be determined.

Shulman *et al.* (137 to 139) have studied the nuclear magnetic resonances of ^{69}Ga, ^{71}Ga, ^{121}Sb, ^{123}Sb and ^{115}In in gallium antimonide and in indium antimonide. The broad lines observed are explained in terms of spin-spin

interactions of the nuclear exchange type. The interaction is sensitive to electron energy states in both the valence and conduction bands. It is particularly sensitive to energy surfaces far from the Fermi level and hence provides information about the band structure in these normally inaccessible regions.

Metals and Semiconductors.—Holcomb & Norberg (140) have measured nuclear resonance in metallic lithium, sodium, and rubidium. They have measured the spin-lattice relaxation time T_1 and the spin-spin relaxation time T_2. Over a considerable range of temperature T_1 is determined by interaction with the conduction electrons. Information is obtained about atomic self-diffusion. There are unusual broadenings at the melting point. T_2 decreases but T_1 does not. This may be due to local magnetic fields from structure imperfections.

Sogo & Jeffries (141) have determined the nuclear magnetic moments of ^{103}Rh and ^{183}W from measurements on metal powders.

Redfield (142, 143) has measured the spin-lattice relaxation times of ^{27}Al in pure aluminum and of ^{63}Cu in pure copper. He finds that the real part of the magnetic susceptibility (the dispersion signal) does not saturate at the same level as does the imaginary part (the absorption signal). Increasing the modulation field from fourteen to forty-one cycles sec.$^{-1}$ causes the dispersion phase to lag because the modulation period is comparable with T_1. He observed large dispersion signals for ^{23}Na in NaCl above saturation. These results are in conflict with the theories of Bloembergen, Pound and Purcell and of Bloch. Redfield finds that the assumption of a spin temperature is not valid because the phases of the spin states are not incoherent. An applicable theory is developed. The phenomenon of rotary saturation is discussed by Redfield. An audio frequency field is applied in the direction of the static magnetic field. One observes the dispersion derivative at resonance with a large rf field, H_1. When the audio frequency reaches γH_1 the dispersion signal goes through a minimum. This not only gives a convenient method of calibrating rf fields but gives a simple way of studying spin systems in small magnetic fields.

Kjeldaas & Kohn (144) have measured the Knight shift in metallic sodium. This shift in nuclear resonance frequency arises from interaction of nuclei and conduction electrons. The average probability density of conduction electrons at the nucleus may be calculated from the results, and it it found to be in good agreement with the theoretical value of Pines. The volume dependence of this probability is small, and this rules out the possibility that Knight's observation of a large low-temperature anomaly is due to a phase transformation. Friedel (145) has discussed the Knight shift in alloys.

Spin-echoes.—The nuclear resonance method based on the echo signals which follow the subjection of a system of nuclei to pulses of rf power continue to be the subject of theoretical and experimental investigation. Bloom *et al.* (146) have now extended the method to the case of quadrupole reso-

nance arising from transition of the nuclei between various energy states of the interaction of the nuclear electric quadrupole moment with electric field gradients in molecules or crystals. Best modulation effects are exhibited by the free precession signals in a small constant external magnetic field. They have verified their theory by experiments on sodium chlorate. The theory of such echoes has also been treated by Das & Saha (147).

The discussion of large numbers of pulses and their corresponding echoes has been carried out by Bloom (148), Das & Roy (149), Anderson *et al.* (150) and Crawford (151). The particular case of four pulses has been analyzed in great detail. Anderson *et al.* have studied spin echo serial storage memories and have discussed the case of a thousand pulses in a glycerine-water mixture. They have discussed the limitations on such a memory device and have considered the effects of superimposing static magnetic fields.

Rothstein (152) has discussed the theory of the significance of nuclear spin echo experiments for the foundation of statistical mechanics.

Lowe *et al.* (153) have used the spin-echo method to study relaxation times in polyethylene. Das & Roy (154) have shown how spin-echoes may be employed to determine crystal structure information. Nolle (155) has studied proton relaxation times in solutions of polyisobutylene in carbon tetrachloride as a function of concentration.

New Applications.—Holder & Klein (156) have measured isotope abundance ratios of hydrogen and lithium by measuring nuclear magnetic resonance intensities. Feher & Knight (157), Klein & Holder (158), & Reilly, McConnell & Meisenheimer (159) have measured magnetic susceptibilities by means of nuclear magnetic resonance techniques. All the methods are based on the fact that different shapes or orientation of vessels containing the sample will produce different demagnetizing factors for the nuclei imbedded in it and therefore will produce shifts of the resonance position depending upon the susceptibility of the medium. They used crossed capillaries, a vessel with two sections of different shapes, and an annular vessel respectively to produce a double resonance line based on the above mentioned effect, such that the splitting measures the susceptibility of the medium. Waters (160) has measured the earth's field by proton resonance. The protons were initially polarized at right angles to the earth's field. Then the polarizing field was switched off non-adiabatically, and the residual magnetization precessed freely in the earth's field inducing a signal in a pick-up coil.

Miscellaneous.—Yokota (161) has given a theory of spin-spin relaxation times. Jaynes (162) has developed a matrix method of finding solutions of the Bloch equations.

Van Vleck (163) has discussed the transfer of energy from Zeeman energy to exchange energy. He has pointed out the reasons underlying the concept of two well defined temperatures, the Zeeman temperature and the exchange temperature. The exactness of the definitions of these temperatures is spoiled by crystal field splittings or by appreciable dipolar interactions.

Hahn & Herzog (164) have discussed a diffusion model for nuclear precession relaxation in solids. Brown & Parker (165) have given a theory of energy relations involving magnetic dipole and electric quadrupole interactions. Ramsey (184) has shown that if resonance transitions are induced by a perturbation at one frequency, then the presence of other perturbations at non-resonant frequencies alters the resonant frequency of the first perturbation. The applications to collision narrowing effects are discussed.

Sogo & Jeffries (166) have determined the spin, magnetic moment and electric quadrupole moment of ^{138}La and ^{36}Cl. Collington *et al.* (167) have made a precision determination of the magnetic moment of the proton by comparison of the spin precession frequency and the cyclotron frequency of protons in the same magnetic field. Rice & Pound (168) have determined the ratio of the magnetic moments of ^{71}Ga and ^{69}Ga.

Linder (169) has examined the thermal relaxation times of protons and fluorine nuclei in $CH_2Cl—CH_2Cl$ and $CH_2Cl—CF_2Cl$. Sugawara (170) has studied the distribution of spin-lattice relaxation times of protons in solid hydrogen. Holzman *et al.* (171) have found a ten hour relaxation time for ^{29}Si in Corning purified fused silica. Brown & Williams (172) have studied the ^{39}K resonance in saturated potassium fluoride solutions. Cagnac *et al.* (173, 174) have described an apparatus in which proton resonance is observed down to 0.5 gauss. They have discussed the details of the resonance shape in this region of field.

Overhauser Effect

The Overhauser effect in which saturation of an electronic resonance produces a polarization of nuclei as evidenced by an enhanced nuclear resonance absorption has been investigated by a number of workers. Kaplan (175, 179) has shown that polarization of nuclear spin states by saturating electron spin levels can alter the electronic resonance absorption line shape. Slichter (176) has shown that in case of electron spin saturation the temperature concept is not applicable. He has shown that in a rotating reference frame which cancels out the Zeeman energy the temperature concept is applicable and that in such a frame the Overhauser effect appears in a relatively simple manner. Abragam (177) has discussed the Overhauser effect in non-metals and has surveyed the various ways in which nuclear spins can relax through interactions with electronic spins. Barker & Mencher (178) have discussed the theory of the Overhauser effect. They have also shown that the way in which the Knight shift varies with saturation is different for the free electron or Bloch approximation than for the model of Bohm and Pines which takes exchange and correlation effects into account.

Klein (180) has discussed the principle of minimum entropy production as applied to the Overhauser effect and in this way provides additional insight into the nuclear polarization effects. Barker & Mencher (181) have applied the thermodynamics of irreversible processes to the Overhauser effect.

Gross (182) has discussed the general theory of magnetic resonance saturation.

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SURFACE CHEMISTRY AND CATALYSIS[1]

By L. H. Reyerson

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

Introduction.—The period covered by this review extends from about December 1, 1954 to nearly the end of 1955. There has been no marked change in activity in the field during the year with perhaps a slight decline in the work published on catalysis. However, investigators are attempting further theoretical advances and thermodynamic studies continue in the forefront. New light is thrown on the mechanism of adsorption on specially prepared metal surfaces. A number of sorption studies have appeared in Russian journals but these papers have not been available except in title or abstract form. Some of these investigations appear to deal with the structures of both natural and mixed sorbents. There were also descriptions of the equipment and methods used to study the sorptive capacity of mineral carbons at high pressures as well as the sorption of gases by powdered coal and carbon black. Finally, several papers reported the sorption of several different gases on the surface of clean mercury.

The papers, presented at the *Symposium on the Physical Adsorption of Gases by Solids* which was held at Kingston, Ontario, late in 1954, appeared in the February 1955 issue of the *Canadian Journal of Chemistry*. Several of the nonreview papers of this symposium will be discussed here. Volume VII of *Advances in Catalysis* was published and several of the chapters merit consideration in this survey. In the experimental field much attention has been paid to precise determinations at moderate to low temperatures using well defined surfaces to adsorb rare gas atoms or some of the smaller gas molecules. Authors, of several new theories of physical sorption, presented their own experimental data in support of the theories. The reviewer makes no claim to completeness but has attempted to indicate the major trends developed during the year.

Physical Adsorption

Theoretical.—Several important contributions have been made to the theories of physical adsorption. Halsey *et al.* (1–4) succeeded in developing theories for the interactions of gas atoms and molecules with several types of surfaces. They first investigated the problem of the interaction of single gas atoms with solid surface at low pressures and sufficiently high temperatures so as to avoid (*a*) interactions between the gas atoms, (*b*) multilayer formation and (*c*) possible capillary condensation. Under such conditions they postulate an isolated plane well, composed of a structureless material with hard sphere repulsion for the gas atoms. A bulb filled with a solid having a high area of surface would permit the measurement of the "dead space" volume. Except at high temperatures the true dead space volume will be

[1] The literature survey for this review was concluded in December, 1955.

less than the measured value, the difference indicating the volume of gas adsorbed. Assuming that the attractive energy is due to London forces and using an expression for the London constant due to Kirkwood & Müller (5) it was found possible to develop expressions which permitted the determination of the energy of interaction of the gas atom at the hard sphere distance, and from observed values of the energy this distance could be calculated as well as the area of the surface. In fact, this procedure constitutes a new method of determining surface area of sorbents that is independent of any theory of multilayer adsorption or any estimate of molecular cross section. To test the theory the authors measured apparent volumes at various temperatures for helium, neon and argon on a carbon black; neon and argon on a saran charcoal; neon and argon on a porous glass; and argon and krypton on alumina. Their values of the interaction energies indicate that light rare gas atoms interact strongly with surfaces. Surface areas determined by this method agree well for saran charcoal with BET areas and the areas of other solids seem remarkably close when one considers the methods used.

Having succeeded so well with the simple model the authors (2) proceeded to consider some refined models. They developed theories for capillary surfaces having plane as well as cylindrical walls. The shapes of the curves, plotted in the same manner as in the simple case, were found to change slightly. The effects of the size of the capillary on the apparent area persisted to a greater relative distance for a cylindrical capillary than for one with parallel walls. Next the theory attempts, with reasonable success, to treat the case of interaction with a simple crystal lattice. The theory was applied to three lattice positions which essentially means dividing the surface into three different types: this was equivalent to introducing heterogeneity of a sort. All the apparent areas of the refined models come out greater than unity so that if experimental data were fitted directly to the refined models, the area that would emerge would be less than for the simple model (1). This would reduce the agreement with the BET area shown by the simple model. Additional experiments were reported using the same porous glass as before and a new very high area saran charcoal. Helium, hydrogen, neon, argon, oxygen, and nitrogen were studied on the glass; and helium, hydrogen, neon, argon, nitrogen and methane on the charcoal. The results on porous glass showed a drift to smaller area as the rare gas molecular size increased. The diatomic gases behaved in a similar manner. For the saran charcoal the areas determined by this refined method were much smaller than BET areas. Except for hydrogen, which may have specific interaction with the surfaces, the other gases gave an area about half that of BET. It was suggested that because of the porous character of this sorbent that nitrogen at "point B" in the BET measurements was filling pores instead of forming a monolayer. The area measured by the present theory was not influenced by gas condensation indicating that the BET area for this high surface area solid may be unreasonably large.

In the next paper (3) the theory was extended to the next higher order

interaction, i.e., that between two gas atoms and the surface. Experiments were carried out at a temperature range where important contributions come from isolated atoms and isolated pairs of atoms only. Reasonably close agreement was found between theory and the experiments using argon on carbon black, krypton on alumina, and argon and neon on saran charcoal. The final paper (4) extended the theory to the case of the interaction of a solid and a two component gas mixture. Here experiments were found to be in good agreement with the theory for the systems: argon-krypton-alumina, argon-methane-charcoal, and argon-nitrogen-charcoal. These theories, coupled with the experimental results used to support them, merit careful study by workers in the field.

A new mathematical approach to the problem of surface heterogeneity and its effect on the physical sorption of gases by solids has been developed by Honig & Rosenbloom (6). The theory they present permits the determination of extreme bounds for a given adsorbate-adsorbent system within which the adsorption isotherms must fall if certain assumptions pertaining to the nature of the adsorption process are applicable. In their development they use reasonable assumptions such as: (*a*) adsorption occurs on a fixed number of sites, (*b*) adsorption is limited to a monolayer, (*c*) each site is associated with a fixed adsorption energy, (*d*) no lateral interactions occur between adsorbed molecules, (*e*) each particle is held rigidly to its site of adsorption, (*f*) the distribution of adsorption energies remains unaltered in the adsorption process. On the basis of such assumptions as these the interpolation theory of the authors is used to analyze gas adsorption isotherms. They find that under conditions such as are found in sorption studies there exist two uniquely determined functions which represent extreme functions. By arbitary selection of θ values from experimental data it was found that the two extreme functions would lead to curves representing the upper and lower bounds for the isotherm. In other words, if the isotherm data fall outside of the curves given by the two extreme functions then the observed isotherm data are not compatible with the assumptions made concerning the adsorption mechanism. Experimental errors in the reference points θ will displace the calculated limiting curves from their correct positions. These same authors (7) extended their original theory in such a manner that they were able to place upper and lower bounds on such quantities as N_m, the number of adsorbate molecules required for monolayer coverage and a term related to the maximum value of the adsorption energy. This new theory may well permit investigators to establish the correctness or incorrectness of their assumptions as to the mechanism of the sorption processes they are investigating and the values of some of the quantities involved.

In fact, Aston, Tykodi, & Steele (8) made use of the basic concept of the above theory and developed expressions for a model of a heterogeneous surface with five types of sites without lateral interaction. On the basis of the model the thermodynamic properties including the isotherms were deduced for helium, neon, and argon adsorbed on titanium dioxide at very low temperatures. In all cases the curves for the model fitted the experimental values

quite well, but the heats of adsorption, either measured or calculated, did not agree as well with the curve derived from the model. Considering the simple model, which did not consider lateral interactions, the agreement is close enough to show the value of applying the theory to such measurements. In a later paper from the same laboratory Steele & Aston (9) measured the heats of adsorption of helium at 14.5°K. on TiO_2 and on TiO_2 plus a one-half layer of preadsorbed argon. The work also included some measurements by Tykodi and Aston at 17.1°K. Heats of adsorption were plotted against the actual numbers of molecules (atoms) V_a adsorbed. The accuracy of the heats at $V_a < .05$ were estimated as ± 30–40 cal/mole. The heats of adsorption of helium on surfaces half covered by argon were below 300 cal/mole at low coverage while they start above 600 cal/mole on the bare TiO_2 surface. The surface half covered by argon showed little evidence of the marked heterogeneity of the bare surface so that argon must smooth out surface roughness. This investigation would seem to confirm the theory of the simple model (g) which postulated that the high energy sites for adsorption were due to topographical heterogeneity; that is surface cracks and roughness where a surface atom can realize two to three times the energy of adsorption of that on a plane surface.

Interesting use was made of this experimental method by Singleton & Halsey (10), when they studied the sorption of argon on carbon black surfaces and then on carbon black surfaces having presorbed layers of xenon on them. They were seeking support for their theory predicting a finite adsorption limit for substances which are solid in the bulk phase at the temperature of adsorption. The finding of this upper limit to the thickness of the adsorbed layers when the temperature was low enough so that the bulk phase of the adsorbent was solid differs markedly from the typical case of rather limitless adsorption as the pressure approaches saturation for those materials that are liquid in the bulk phase. They develop a theory for this finite limit, in terms of the excess forces at the surface and the incompatibility of the crystal lattices of the adsorbent and adsorbate. The degree of incompatibility necessary to suppress growth beyond a few layers does not appear to be large. Reasonable agreement was found between theory and the experimental results for krypton and graphitized carbon black at 77.1°K.

The plotted data for this isotherm showed the definite stepwise character attributed to a homogeneous surface and the theoretical curve produced the same series of steps. Plots of the data for the sorption of argon on anatase and silver iodide at 77.1°K indicated that argon was not compatible with these surfaces. When these surfaces were coated with as much xenon as they would support the compatibility of this surface for argon was increased. Thus, xenon formed a sort of "graded seal." The authors expanded their theory to cover the adsorption on top of preadsorbed layers and found good agreement between the limiting isotherm and the experimental data for the sorption of argon on graphitized carbon black having multilayers of preadsorbed xenon. The agreement was not so good between the calculated intermediate isotherm and the data. The theory emphasizes a new concept

with respect to the state of the adsorbate on the surfaces of solids when it is a solid in the bulk phase. On the other hand, an extrapolation formula applicable to smooth isotherms at high coverages was shown to be analogous to the Harkins-Jura equation.

The problem of multilayer step adsorption was interpreted by Hill (11) from the point of view of corresponding states in different layers. He showed that the second and third layers of krypton on graphitized carbon black and the higher layers of argon are "normal" in this sense. He suggested that the Ising model for a two dimensional hexagonal lattice ought to apply to this problem. The principle of corresponding states can be used to furnish "unperturbed" or "reference" behavior with which the actual location of successive steps may be compared. The argument is independent of any model of an adsorbed layer but is more nearly applicable, the sharper the steps, the lower the temperature, and the more uniform the surface. This development should be considered as supplementary to the earlier discussions of Halsey *et al.*

Proof of true reversibility in physical adsorption of gases on solid surfaces has been sought by many investigators in the field. Pace and coworkers (12) attempted to establish the fact by applying thermodynamic methods in proving their case for the systems studied. They derived the same thermodynamic quantities from independent measurements of adsorption isotherms, heats of adsorption and heat capacities at several surface coverages and temperatures. Calorimetric heats of adsorption and heat capacities of methane adsorbed on rutile were measured between 80 and 140°K. The measured heat capacities of the methane adsorbed on rutile checked very well in the values calculated from the temperature coefficient of the various heats of adsorption. The authors considered this to be strong evidence of reversibility for this system, at least at the higher temperatures. Heats of adsorption of argon on rutile were determined between 60 and 90°K. The data obtained at the three higher temperatures were used with measured heat capacities to construct a single curve at 63.5°K. The values measured at this temperature did not fall on this curve indicating that the sorption of argon did not take place reversibly below 73°K. The result of the zero point entropy determination for the adsorption of krypton on rutile ($\theta = 0.57$) gave a value of 0.41 ± 1.0 deg^{-1} mole^{-1}. In view of the precision attained it was found impossible to clearly decide whether or not the zero point entropy was zero at the absolute zero. A zero entropy would be strong indication that the adsorption process was reversible. A small positive value on the other hand could arise from an appreciable number of molecules being present in a reasonably homogeneous but not completely filled group of sites at very low temperatures. The character of the rutile surface suggests this possibility. It would seem that additional evidence must be presented before true reversibility of physical adsorption can be accepted for any but special cases. The methods here used may well find wider application in attempting to prove the case.

When considering the treatment of non-cooperative adsorption of a gas

on a heterogeneous surface Hepler (13) raised a question as to the best choice of limits for the integration of the isotherm equation for total surface coverage. He pointed out that the integration from $-\infty$ to $+\infty$ as carried out by Halsey & Taylor (14) gave rise to an uncertainty which could be resolved by determining whether the integral from $-\infty$ to 0 contributes appreciably to the total integral. His proof showed that for the cases studied this part of the total integral always turned out to be small, except in the high pressure range. Thus, the integration over the total range is not likely to be very seriously in error except at high pressures. Hepler (13) does however, develop correction terms that could be used. He also drived a direct relationship between the distribution function of adsorption energies and the heat of adsorption. The derived equation was shown to have the advantage of being valid, for this particular case, for high and low as well as intermediate pressures. Expressions for the total integral heat and the differential isothermal heat of adsorption related them to the distribution function. The differential isothermal heat of adsorption q_T was shown to be equal to the isosteric heat q_{ST}. There is disagreement with the conclusions of previous authors because q_T in these derivations does not include any heat of compression. In concluding this section on the theoretical developments for the year mention should be made of the note by Honig (15) which provides a general solution of the equations of Honig & Hill (16) concerning the determination of the adsorption energy heterogeneity of solid surfaces.

Experimental.—Much of the experimental work on adsorption which appeared in publications during the year fell naturally into two areas. The first consisted of sorption studies on various carbon surfaces with little or no chemisorption being observed. The second dealt with studies using metal films, reduced metals and their oxides. Chemisorption was often found in this area of investigation and most of the work on metal films will be dealt with in that section. Working with highly graphitized carbon black Ross & Winkler (17) studied the monolayer adsorption of argon and nitrogen at 77.8°K and 90.1°K. In the low pressure range these gases showed two dimensional ideal gas behavior giving straight line isotherms. As the pressure increased the behavior of the gases could be described by a two dimensional van der Waal's equation. Above 50 per cent coverage the isotherm has the form of a Langmuir equation, indicating the sorption of a mobile film on localized sites. The results gave good evidence for a surface with no significant energy differences and supported the views of Halsey (10) that these carbon black surfaces were very homogeneous. Ideal gas behavior in the monolayer was observed for a considerable portion of the isotherms. The straight line isotherms for low pressures passed smoothly into curves convex to the pressure axis which was what would be expected of a mobile adsorbed film. The calculated isosteric heats, while approximate, indicated a constant value up to $\theta = 0.10$ after which they rose linearly to $\theta = 0.50$ and then remained constant to $\theta = 0.90$. The same authors (18) worked with krypton on the same black and found the critical temperature for condensation of the monolayer to be about 82°K. At 90.1°K. the curves were similar

to those for argon and nitrogen, whose calculated two dimensional critical temperatures lay below the temperatures of measurement. On a similar carbon black at 70.2°K. Clark (19) carried the isotherms of krypton to higher relative pressures and established equilibrium by desorption measurements. A stepwise isotherm was found with risers indicating vertical discontinuities in both first and second layer adsorption. Pressures calculated by the theory of Singleton & Halsey (10) agreed well with the experiments. Calculated isosteric heats agreed well with those found by Amberg, Spencer & Beebe (20) who measured the heats of adsorption of krypton on a similar highly graphitized carbon black at 90.1°K. These authors also found a pronounced step-wise isotherm and their heat curves showed a definite change at monolayer coverage with a lesser change at the completion of the second layer. The isotherms as well as the heat data pointed again to the homogeneous character of the surface of this special black.

In recent years several laboratories have prepared very high area charcoals from saran, a polyvinylidene chloride. The chlorine complex was removed by heating in hydrogen. This charcoal developed increasingly high surface areas on activation with steam. Culver & Heath (21) have prepared a series of these saran charcoals of varying degrees of activation and studied the adsorption of nitrogen at 77.6°K. and ethyl chloride at 0°C. on them. The isotherms, carried to saturation, showed that the most highly activated charcoals had the greatest sorptive capacity. Average pore radii appeared to be 7–8 Å and they were only 10 to 15 per cent greater for highly activated samples. Point *B* values gave monolayer areas of about 1000 m^2/g for the unactivated charcoals and about 3000 m^2/g for the most highly activated. The authors claim these values are consistent with density determinations and screening effects. On measuring the isotherms of N_2 at 90.4°K. and ethyl chloride at 18°C. the authors (22) calculate the differential molar heats of adsorption. These values fall with increased coverage for all the charcoals even though activated to different degrees. As saturation is approached the heats rise for N_2 and they rise and then fall again for ethyl chloride. While the curves for the heats plotted against the fraction of saturated adsorption are all similar for a given gas, the values for the most highly activated charcoal lie below those for the less activated material. Other thermodynamic values for these sorptions are discussed and from these it is concluded that more uniform surfaces exist in the most highly activated charcoals. Since the pores of these saran charcoals are considered to be comparable in size to simple hydrocarbon molecules Dacey & Thomas (23) pyrolized adsorbed vinylidene chloride monomer within the pores in order to block them or change their structure. After this treatment such gases as nitrogen and argon were adsorbed slowly. The rate of adsorption increased rapidly with the temperature. A method was developed for determining the energies of activation of the process by altering the temperatures during one experiment. The pore volume was found to decrease only by an amount roughly equivalent to the space required for the weight increase produced by the pyrolized material.

MacIver & Emmett (24) produced another unusual carbon black by decomposing CO over an iron catalyst at 450 to 600°. The carbon of thread-like character was separated from the massive catalyst and N_2 areas determined at −195° before and after reduction with H_2. These adsorption-desorption isotherms lacked hysteresis, indicating the absence of pores in the range 20–1000 Å. The BET area was found to be 145 m^2/g before reduction and 144 m^2/g afterwards. This indicated a diameter of 132 Å for the threads with a roughness factor of five, while their apparent thickness was 500–1000 Å. Carbon monoxide isotherms indicated chemisorption probably on traces of iron. If so, then 7 per cent of the carbon surface was iron. X-ray studies checked this, provided the Fe had a reasonable roughness factor. Dietz and his co-workers (25) continued their nitrogen adsorption studies on bone chars and activated cocoanut charcoal at three temperatures between 69° and 90°K. At low pressures a steady state was reached only after hours of time. Isotherms tended to become coincident above a relative pressure of 10^{-2}. As has been reported often by other investigators, the BET theory was found to apply to sorptions on the bone chars at relative pressures from .05 to .35. Monolayer areas on the chars, determined from BET plots, appeared to increase with a decrease in temperature. The data for the charcoal did not fit BET theory but gave a good Langmuir plot for $P/P_0 =$ 0.2 to 0.8. This work suggests that the range of pressures studied may be important in determining the nature of the predominant forces. The adsorptions of ethylene and perfluoroethylene on an active charcoal, were measured by McDermot, Arnell, & Lawton, (26) from 273.2° to 308.5°K. The heats of adsorption of the perfluoroethylene were consistently higher than for ethylene but only by an amount to be expected from the difference in molecular weights. Entropy calculations for adsorbed ethylene agreed with a model in which the adsorbed molecules are mobile and possess at least two degrees of rotational freedom. The isotherms showed no hysteresis for either gas.

Earlier studies of the adsorption of gases on the highly graphitized carbon blacks have concerned themselves primarily with non polar gases, water vapor being an exception. However, Beebe & Dell (27, 28) have begun a series of investigations on the adsorption of polar molecules on carbon blacks which have successively undergone higher and higher heat treatment. Adsorption-desorption isotherms of sulfur dioxide on four of these blacks were obtained at 0°C. A marked difference was observed between these isoterms and those for argon on the same carbons. Heat treatment of the carbons has little effect on the argon adsorption, while heating to 1000° markedly reduced the amount of sulfur dioxide adsorbed. The isotherms for sulfur dioxide on the carbons heated to 1500° and 2700° changed very little from that on carbon heated to 1000°. Since most of the oxygen incorported on the surface of the unheated black was removed by heating to 1000°, it was concluded that the loss of this oxygen greatly reduced the capacity of the blacks to adsorb sulfur dioxide. Differential heats of adsorption were measured on these blacks, and the plots of these heats against relative pres-

sure showed striking differences. On the untreated carbon black of high surface oxygen content, the calorimetrically measured heats fall steadily from an initial value of 15 kcal/mole to values approaching the heat of vaporization. On the black heated to 2700°, having a surface free from polarizing complexes, the differential heats start at 6 kcal/mole, rise to a maximum at 7.4 kcal/mole, and then decline. The maximum occurs somewhat below monolayer coverage, suggesting that second layer formation begins before the monolayer is completed. The heat values for the carbon treated at 1000° were intermediate between these extremes. On the high temperature carbon there was no sharp separation between first and second layer formation and van der Waals attractive forces overshadowed lateral dipole repulsions.

Ammonia was the second polar gas studied and isotherms on these same blacks were measured in the temperature range of −78° to −22°. The untreated black adsorbed ammonia more strongly than the heated ones did. However, the heat treated blacks had very little attraction for the ammonia molecules with the result that the isotherm was convex to the pressure axis up to 0.5 relative pressure. The heats of adsorption on the highly graphitized black were found to be virtually constant at all coverages and were approximately equal to the heat of vaporization. The values were considerably higher for the untreated carbon and never did closely approach the heat of vaporization. These results are similar to those obtained by Millard *et al.* (29) who measured the heats of adsorption of water on the same untreated carbon black (Spheron 6) and on one graphitized black. The heats of adsorption on Spheron 6 were above the heat of liquification of water while on the heat treated black they were lower. These studies indicate the profound effect that changes in the properties of similar surfaces may have on adsorption phenomena.

Interesting observations were made by Barrer & Strachan (30) when they studied adsorption on and diffusion through micro porous cylinders of compressed carbon powder having high internal surfaces. Argon was adsorbed on the uncompressed carbon at 78° and 90°K. without hysteresis, while at some compression of the carbon the type of isotherm changed showing definite hysteresis. This disappeared at still higher pressure. Measurements of surface and volume diffusion indicated that dilute films of helium, neon and hydrogen might be regarded as one or two dimensional gases. Argon, kyrpton and nitrogen appeared to give localized adsorbed films with surface flow proceeding by jumps, each unit requiring an energy of activation a little greater than half of that of the heat of adsorption. Thus, surface flow may well be important in the transport of matter through micropore structures. Additional attempts at determining the changing character of the homogeneous surfaces of graphitized carbon black during surface oxidation were made by Healey, Yu, & Chessick (31). These authors claimed that oxidation changed a part of the hydrophobic carbon surface to one that is more hydrophilic. The ratio of the apparent area available to water adsorption to the total area as determined by nitrogen adsorption was taken as a

measure of the surface oxidized. The nitrogen area almost doubled during oxidation while the adsorption of water indicated that about one-eighth of the surface had become hydrophilic. Part of the hydrophilic sites were destroyed on high temperature activation. The modification of the carbon surfaces was obviously complex so that the rate of increase in hydrophilic sites could not be taken as the rate of total oxidation.

A number of rather unusual solids were studied as adsorbents during the year. Dacey, Smelko, & Young (32) measured the sorption of nitrogen at −183°, −78° and 0°C., and of hydrogen at −183° on an unusual but stable clathrate compound $[(CH_3)_3As \cdot PdCl_2]_2$. This needle like compound contains cylindrical tunnels in the crystal lattice and there should be one cell per molecule. Nitrogen was sorbed on the whole needles so slowly that the material was pulverized in an agate mortar in order to open up the tunnels to the gas. The maximum possible sorption of 40 cubic centimeters at standard pressure and temperature was never even approached. Hydrogen was sorbed quite rapidly at −183°C. but the rate was too slow for nitrogen at this temperature so that it was studied at −78°C. It seemed probable that the pore system was never saturated in these experiments so that sorption on the inner surfaces was not very revealing.

Garden, Kington & Laing (33) also sought to examine the equilibrium properties of intracrystalline sorbed phases. They measured the heats of sorption, isotherms and the entropies of argon at 90°K in natural and calcium chabazites, the latter prepared by exchanging calcium for the sodium in the natural product. It was believed that an intracrystalline sorbed phase in a rigid host lattice would come closer to idealized adsorption because such a system would eliminate surface and edge heterogeneity and multilayer formation, as well as reduce mutual interaction between sorbed molecules. Isosteric heats of sorption of argon in chabazite were shown to be 3800 cal/mole with a maximum value of 3820 cal/mole and a minimum value of 3675 cal/mole between $\theta = 0.05$ and 0.88. This variation is less than that observed for sorptions on the exterior of small crystals. Curves obtained by plotting heats of adsorption against the fraction of the surface covered showed rather regular differences between the two minerals, with higher heats being observed for the calcium chabazite. Differential and molar entropies showed similar differences. The sorption of gases on inner crystalline surfaces opens up interesting possibilities.

Another interesting adsorbent, calcium halophosphate, was used to measure the sorption isotherms of krypton. Corrin & Rutkowski (34) found marked discontinuities in the isotherms under certain conditions but observed smooth ones under other conditions. They concluded that the smooth isotherms represented equilibrium conditions but they also noted that the time allowed for the adsorption of the first increment had a marked effect on later points on the isotherm. The values obtained after long contact with the first increment of gas could represent some supersaturation phenomenon instead of an equilibrium. This work suggests that any measurements yielding isotherms having discontinuities be carefully checked.

Water vapor was used as the adsorbate in only a few studies. Law (35) determined the sorption of H_2O on germanium and germanium oxide surfaces in an attempt to find out why germanium junction devices were so sensitive to this vapor. Isotherms measured at about 300°K. were found to be multilayer over most of the pressure range. The monolayer filled at less than 0.1 P_0 and 8 to 10 layers were sorbed near saturation. On GeO_2 the monolayer is also complete at low pressures, but the amount sorbed above 0.3 P_0 is about half that on the metal. Multilayer sorptions were reversible down to the monolayer when heat was required to remove the water. This resulted in a reaction between Ge and water forming an oxidized layer that acted like the GeO_2. Thermodynamic calculations indicated that there were strong localized adsorptions in the monolayer but that after the first two layers had formed the upper layers were mobile and the heat of adsorption coincided with the heat of condensation of water. The electrical properties were not affected until the third water layer, having high molecular mobility, had been sorbed. When this is desorbed to about a monolayer the electrical properties of germanium returned to normal.

Further studies by Razouk & Mikhail (36) were reported on the sorption of water vapor on magnesium oxides prepared by dehydrating brucite at temperatures from 350° to 1100°C. Oxides prepared below 650°C. rehydrated stoichiometrically but above that temperature the uptake diminished until the oxide prepared at 1100°C. no longer took up water. The oxide heated below 650°C. sorbed water throughout its porous structure at 35°C. and this was followed by chemical reaction. Desorption at 35° removed only about two-thirds of the water and this same fractional removal was found for the oxides prepared at higher temperatures. Heating to 350°C. removed all of the sorbed water. Sorption gave a sigmoid isotherm but the authors did not suggest any real mechanism for the process. The question as to whether or not this was truly a sorption process should be raised.

Several additional studies of interest should be mentioned before leaving this section on physical adsorption. Zettlemoyer *et al.* (37) prepared an oxide coated nickel powder and studied the sorption of argon on it at −195° and −183°C. This was repeated after four successive reductions with dry H_2 at 350°. The isotherm on the unreduced powder differed from those on the reduced nickel powder in that monolayer coverage was reached at higher relative pressures. The isotherms for the four reduced samples coincided when the sorption values were reduced to unit area. The results indicated a surface that was very heterogeneous with respect to energy sites. In the light of Beecks earlier work and the recent work of Rideal reported here it would seem possible that the sorption on the reduced nickel powder might well be on a nickel surface that had chemisorbed hydrogen atoms on it. Walker & Rusinko (38) prepared an iron powder by heating iron carbonyl. The powder consisted of spherical particles 10μ in diameter. They obtained isotherms for argon, nitrogen and carbon monoxide on this powder at −195°C. Type II isotherms were obtained. Those for carbon monoxide were essentially parallel to those for argon and nitrogen, but the sorption was greater by a uniform

amount. Hysteresis was observed on desorption in some cases. However, the authors were not able to characterize the surface of the powder nor the mechanisms of adsorption.

Dielectric measurements carried out during the sorption process have not achieved the success hoped for in attempting to follow the process of adsorption. Channen & McIntosh (39) measured capacitance changes as volumes of adsorbed gas increased on silica gel and rutile surfaces at several temperatures. Butane, water vapor and ethyl chloride were studied on silica gel, while butane, sulfur dioxide, ammonia and ethyl chloride were used with rutile. Butane was also sorbed on silica gel having several different water contents. A break in the capacitance curves was observed in all cases except for butane on rutile. The authors called the breaks the critical values of the volume adsorbed. The breaks were found near monolayer coverage on the rutile surfaces except for butane, but this was not so for silica gel. Since attempts to compute the dielectric constants did not meet with success, it was concluded that up to the present no satisfactory method had been found for obtaining the apparent electrical properties of adsorbed matter. Waldman & McIntosh (40) extended the frequencies up to 100 mc/sec in their attempts to find anamolous behavior in the phenomenon of dispersion in adsorbed molecules. No marked change was observed over that at low frequencies. The problem posed thus is not yet answered.

Chemisorption

Until recently, following Langmuir, the general assumption has been that chemisorption on clean surfaces was determined by the rate at which molecules from the gas encountered vacant sites on the surface. Erlich (41) suggested a new theory which postulates that before a gas molecule may be chemisorbed it must be physically adsorbed. He proposed (*a*) that the rate of chemisorption was determined by the frequency of successful collisions of physically adsorbed gas molecules with the substrate, (*b*) that the physically adsorbed molecules were in a steady state, and (*c*) that chemisorption occurred at fixed sites on a surface not subject to thermal disorder. The physical situation of (*a*) would be that in the limit of zero coverage the rate of impingement (the condensation coefficient appears to be unity for the cases considered except for hydrogen and helium) exceeded the rate of chemisorption, provided chemisorption is not limited to a small number of sites. The latter situation should be recognized in as much as once these sites are filled chemisorption, if it proceeded at all, would be limited by the new step of the diffusion of the chemisorbed species away from their sites. Initially clean metal surfaces would satisfy suggestions (*b*) and (*c*). Erlich uses the chemisorption of nitrogen on tungsten from the work of Becker and Hartman but the evidence in support of the new concept is scanty. The kinetic formalism for chemisorption is of course changed when the presence of physically adsorbed molecules is taken into account. This does not necessarily affect the equilibrium state, for a complete consideration of the

equilibrium process by this theory gives the Langmuir expression for the adsorption of a diatomic gas except for differences in the constant of proportionality. Further experimental proof will be needed to establish the merit of this concept.

Most of the experimental work on chemisorption had to do with metals and metal oxides. Baker, Jenkins & Rideal (42) prepared nickel films after the manner of Beeck and studied the adsorption of hydrogen in the ranges of temperature and pressure investigated by Beeck (43, 44). This study does not support the suggestion of Beeck that the slow uptake of hydrogen, after the initial rapid chemisorption, is due to the solution of hydrogen in the nickel but it does definitely indicate that the added reversible adsorption is also chemisorption on lattice vacancies or spaces between macrocrystals. The added uptake involved an energy of activation. Rideal *et al.* suggested that the secondary slow uptake could well be on interior sites but that the first sorbed hydrogen could not migrate or diffuse to these sites at −183°, but this became possible at 20°. Their experiments showed an additional uptake of hydrogen at 20° and higher pressures, and cooling to −183° trapped this gas. However, evacuation at 20° was found to remove hydrogen from the surface and buried sites so that cooling to −183° again gave the same isotherm as was obtained originally at that temperature. This work seems adequately to answer a number of questions raised by Beeck and others studying the adsorption of hydrogen on metal films. Using the same nickel films Baker & Rideal (45) studied the sorption of carbon monoxide at −183° and 10^{-3}mm. pressure. Using chemisorbed hydrogen as a standard they found that one molecule of carbon monoxide was chemisorbed on one atomic site in contrast to the two sites occupied by hydrogen after dissociation into atoms. At higher temperatures the heat of sorption fell steadily from 35,000 cal/mole at $\theta = 0.74$ to 4,500 cal/mole at $\theta = 1.0$. At higher pressures than 10^{-3}mm. and at −183° a small amount of additional sorption took place, but since the heat was about 4000 cal/mole it was concluded that this was physical adsorption. At −183° on a chemisorbed hydrogen substrate, carbon monoxide was able to form a surface complex containing both gases. At 20° carbon monoxide was sorbed on vacant sites and hydrogen was also displaced up to 85 per cent of the amount on the surface. The residual hydrogen appeared to be more strongly bound. When the system nickel film plus sorbed carbon monoxide was heated from 21° to 150° desorption occurred, followed by slow adsorption and the production of carbon dioxide and a carbide. The velocity of this reaction was dependent upon the diffusion of the carbide into the substrate. Hydrogen was not able to displace chemisorbed carbon monoxide but adsorbed carbon monoxide retarded the sorption of hydrogen to inner sites not accessible to carbon monoxide. These studies may have important implications for work on catalysts.

The chemisorption and interaction of oxygen with clean metal surfaces was extensively studied by Lanyon & Trapnell (46). Isobars were obtained at temperatures of −183°, −78° and 0° for the sorption of oxygen, hydrogen

and carbon monoxide on evaporated films of Rh, Mo, W, and Fe, of oxygen and carbon monoxide on Ta, Pt, and Pd, and of oxygen on Cu, Zn and Al. On the latter three metal films sorption was also studied at 100°. On Rh, Mo and W at −183° rapid sorption of oxygen and hydrogen resulted in chemisorbed monolayers having one atom per surface atom. On Ta, Pt, Pd, Cu, Al and Zn, oxygen—and on Fe, hydrogen—formed similar monolayers; but on Fe, oxygen formed several layers of oxide. On Rh, Mo and possibly Ta the fast chemisorption of carbon monoxide corresponded to a two site mechanism while on W and Fe it appeared as though the carbon monoxide occupied between one and two sites. On Pt and Pd a single site sorption seemed probable. Following the fast sorption of oxygen the kinetics of slow uptake were followed on Rh, Mo, W, Ta, Fe, Cu and Zn. In the cases of Rh, Mo, W, Ta and Zn it was believed that the formation of the first oxide layer had been observed. It was suggested that the chemisorbed oxygen atoms interchanged with underlying metal atoms whereby the metal atoms were exposed to further oxidation. On Cu and Fe, formation of as many as six to ten oxide layers was observed. Derived rate expressions were interpreted in terms of the theory of Cabrera and Mott which suggests mobility of atoms induced by the electric field which exists across the oxide layer. Penetration of the lattice itself was offered as a more satisfactory explanation and this would mean the interchange of sorbed oxygen atoms. Another possibility would be the migration of defect sites. Rate studies for the uptake of oxygen on Rh, Mo, W, Ta and Zn gave the same kinetic law and the reaction order was found to be 0.5 for all of these metals. The fact that carbon monoxide occupied two sites on most of the metals instead of an expected one site raises the question as to its usefulness in determining the surface area of a reduced metal oxide that is free metal. Teichner & Morrison (47) raised this same question in connection with their studies of the sorption of gases on stoichiometric and nonstoichiometric (excess of oxygen) oxides of nickel. At low temperatures both carbon monoxide and oxygen appeared to be chemisorbed. The green stoichiometric oxide turned black when oxygen was admitted. The chemisorbed product of both carbon monoxide and oxygen seemed stable at room temperature but both could be removed by evacuation at 200°. These results differed from previous work on the oxide films on nickel. In both cases, however, these gases never covered the surface by more than 25 per cent of the monolayer. At least twice as much carbon monoxide was sorbed on these oxides than was oxygen. This was the reverse of what was found in the earlier work. The conclusion reached for one type of the oxides of nickel cannot be safely applied to other types.

In attempting to further elucidate the mechanism of chemisorption and reaction of carbon surfaces with oxygen Loebenstein & Deitz (48) preheated three bone chars, a cocoanutshell charcoal and a carbon black in a stream of nitrogen at 400° for 24 hours. Oxygen was then chemisorbed at 200° in a closed cyclic system with the combustion products remaining in the system. Quantitative recovery of the oxygen was obtained by summation of the

analyses of (*a*) combustion products (*b*) desorption products from a stream of nitrogen passed over the carbons first at 200° and than at 400°. The character of the chars or carbons determined the ratios of combustion products to desorbed oxygen products at the two temperatures. It was suggested that the chemisorbed oxygen complexes could be made to decompose either at high temperatures or by passing inert gases over the chemisorbed material at the pretreatment temperature of the carbons. Surfaces of such material are so complex that it is surprising that the recovery of oxygen, as free gas or in the compounds formed, was so nearly complete.

Miscellaneous

Interest has continued in the behavior of polar gases toward a variety of proteins. Benson & Richardson (49) obtained sorption-desorption isotherms at 25° and 40° for water, ethyl alcohol, ethyl ether, and ethyl chloride on native and heat denatured proteins. Egg albumin and bovine plasma albumin bound the vapors in the following order: H_2O, EtOH, Et_2O, EtCl. Sorption decreased as the adsorbate became more restricted in its ability to form hydrogen bonds. The same trend was observed with heat denatured egg albumin. The series MeOH, EtOH, and *i*-C_4H_9OH on egg albumin at 25° showed a marked decrease in the amount of sorption with increasing size of the adsorbate molecules. All of the isotherms showed characteristic hysteresis loops and these were quite reproducible. Peterson & Reyerson (50) chose to study the sorption of HCl by crystalline insulin at 20° and −78.9°. Sorption was found to require from three to ten days per point. Hysteresis was found on desorption and at 20° about 50 mg. of HCl per g. of insulin was permanently bound at zero pressure. At −78.9°, 215 mg. were bound per gram of the insulin. The permanent binding of the HCl seemed to be strongly temperature dependent. As yet the use of proteins as adsorbents for polar gases has not been too revealing as to the sites and the character of the process.

Catalysis

No decided change in the trend in the fields of investigation was noted during the year. The third volume in Emmett's series on *Catalysis-Fundamental Principles* (51) appeared. This volume deals with hydrogenation and dehydrogenation; all phases of the subject are well covered, with about a third of the book devoted to the important subject of the synthesis of ammonia. Trapnell (52) gave an excellent summary of the present day knowledge of the factors which can cause variation in activity among different metal catalysts toward the same chemical change. He compared the geometric factors of surface structure, the electronic character of the metals, and the influence of the work function of the metals used as catalysts. At the June 1954 meeting of the *Societe de Chemie Physique* an extended discussion was held on the subject, *The Structure and Texture of Catalysts*. The many papers with the full discussions which followed were published later that year (53). The investigations reported at this meeting covered a wide range

of work on the structure of catalysts with special attention being paid to surface characteristics. The seventh volume on *Advances in Catalysis* (54) devotes several chapters to the behavior of semi conductors and metals in chemisorption and catalysis. The electronic factor and electronic interaction between a solid and the chemisorbed molecules come in for careful discussion.

Isotopes continue to be used in furthering knowledge of the mechanism of the reactions on the surface of catalysts. Using a mass spectrometer, Anderson & Kemball (55) followed the reaction of deuterium and aliphatic alcohols over evaporated metal films of Ni, Fe, W, Rh, Pd, and Ag plus a Fischer-Tropsch catalyst and a form of zinc oxide. In most of the experiments they used methyl and ethyl alcohol vapors; isopropyl and *tert*-butyl alcohol were tried in a few cases. The hydroxyl hydrogen always exchanged more rapidly with a lower energy of activation than the aliphatic hydrogens. Extensive multiple exchange was found only on rhodium and the Fischer-Tropsch catalyst at higher temperatures. The metals showed the same order of exchange activity as has been found for the hydrogen of ammonia. The order differed for the exchange of aliphatic hydrogen. Deuterium and methyl alcohol were adsorbed comparably on the nickel film.

Similarly Rowlinson, Burwell & Tuxworth (56) followed the exchange of deuterium with saturated hydrocarbons on nickel films and reduced nickel oxide catalysts. The results were found to be similar for both types of catalysts. The isotopic exchange proceeded favorably at 150°–200° to produce a mixture of species having one to all of the hydrogens exchanged. With heptane and 3-methylhexane, the most aboundant species were those of extensive but not total exchange. The deuterium was most fully exchanged with cyclopentanes, cyclohexanes and 2-3-dimethylbutane. Only one hydrogenolysis of the C—C bonds occurred and that was with ethyl cyclobutane in which case the rate was comparable to exchange. The data indicated an initial adsorption of the hydrocarbon molecule with the cleavage of a carbon-hydrogen bond. The point of attachment then shifted in an $\alpha-\beta$ process with isotopic exchange accompanying each shift, while α and γ shifts were relatively uncommon. A single branch in the carbon skeleton did not impede migration but a *gem*-dimethyl group blocked it. The similar distribution of the isotopically exchanged species for the different catalysts seemed a little unusual. Taylor (57) prepared films of arsenic, antimony, and germanium on glass and studied the exchange of hydrogen and deuterium with metal hydrides as well as their decomposition. He was seeking confirmation of the concept that chemisorption of hydrogen and perhaps other gases could occur on clean metal surfaces with no energy of activation. Earlier work has indicated that for hydrogen, on a number of metals, energies of activation were negligible and that impurities in the metals might be the cause of higher energies. Such concepts obscured the fact that elements had specific catalytic activity. This work of Taylor's definitely showed that the specific chemical character of the surface was the essential thing. Hydrides decomposed in the presence of deuterium produced no HD, but metal hydrides mixed with metal deuterides did produce HD. These experiments appeared to prove

that chemisorption involved chemistry in each case. These metal surfaces activated the Me—H bond but not the H—H bond or the D—D bond.

Catalytic reactions involving the oxidation of carbon and carbon monoxide were investigated in a number of laboratories. Frey (58) treated charcoals with a number of mineral acids and then studied the oxidation of these over a temperature range of 300°–550° in the presence of radioactive carbon monoxide. He was able to show that the mineral acids had changed the reactivity of the charcoal surfaces so that the ratio of carbon monoxide to carbon dioxide in the products of combustion has risen considerably and this ratio had a positive temperature coefficient which seemed unusual. The acid treatment reduced the adsorption of oxygen but favored the liberation of carbon monoxide. Hughes & Hill (59) were interested in determining the role of vanadium pentoxide in the catalytic oxidation of carbon monoxide. They found heats of activation to be 28.4 kcal for adsorption and 6.2 kcal for desorption. The results indicated that only a small fraction of the surface had the active sites necessary for this oxidation. The chemisorbed carbon monoxide apparently reacted with oxygen atoms of the catalyst and was desorbed as carbon dioxide. Oxygen then acted to regenerate the catalyst. In an attempt to discover whether carbon-oxygen surface complexes played a similar role in reactions involving N_2O, as they do in reactions involving water, Smith & Mooi (60) followed the catalytic oxidation of CO by N_2O over "ashless" carbon black and charcoal at from 300° to 500°. Their results indicated that N_2O and H_2O behaved quite differently as oxidizing molecules for CO over carbon surfaces. Carbon-oxygen surface complexes played an important role in reactions involving water, whereas in the case of N_2O the complexes behaved more like poisons than as reaction intermediates. Both oxidized and reduced chromia catalysts were used by Voltz & Weller (61) in their studies of the oxidation of carbon monoxide at 100°. The reaction rates over both of these catalysts were found to be quite similar. Oxygen reacted with the adsorbed hydrogen of the reduced catalyst forming water which remained on the catalyst. These same authors (62) added potassium oxide to the chromia catalysts and found that its presence decreased the activity of the catalyst for carbon monoxide oxidation as well as for a number of hydrogenation reactions. The potassium oxide appeared to form chromates or dichromates because its presence increased the rate of the decomposition of aqueous hydrogen peroxide, which is known to happen on these compounds.

Several attempts were made to elucidate the character of the acidic surfaces of cracking catalysts and others of this type. Danforth (63) condensed certain methylsiloxanes with aluminum hydroxide and found that definite atomic ratios of silicon to aluminum were formed as a function of the number of available hydroxyl groups on the silicon. The data suggested that the active centers of the silica-alumina catalyst could be represented as a combination of a Lewis acid (three coordinated aluminums) and a Brönsted acid. This proposed structure correlates much of the known data on cracking catalysts. In an ingenious attempt to prove the acid character

of cracking catalysts surfaces, Mapes & Eischens (64) obtained the infra red spectra of ammonia chemisorbed on such a catalyst preheated to 500°. The spectra ought to show whether the surface supplied protons or whether it results from the ability of surface atoms to share an electron pair from ammonia as in Lewis type acids. Characteristic absorption bands for both NH_3 and NH_4^+ were found. The presence of the NH_3 strongly suggests that most of the centers are of the Lewis type where the unshared electron pair of nitrogen fills an electron pair vacancy in the catalyst with little effect on the NH_3 configuration. Even the presence of NH_4^+ did not prove the presence of proton acid centers for the proton could have come from water molecules on Lewis acid centers. Johnson (65) developed a titration method for determining the acidity of solid surfaces such as are found in cracking catalysts. He then used the polymerization of propylene to correlate the acidity with catalytic activity. A linear relation was found between the acidity of silica-alumina catalysts and the propylene polymerization rate at 200°. Another point of view was suggested by Oblad and co-workers (66) in their studies of the reversible adsorption of water by γ-alumina. These authors found considerable heterogeneity on the solid surface after dehydration at 538° and suggested that this could be due to the strains set up in the surface due to removal of hydroxyl groups. Such highly strained surfaces might then activate a number of molecular species thus behaving as catalytic centers.

Interesting observations on a Raney nickel catalyst were made by Smith, Chadwell & Kirslis (67) when they found the hydrogen content of this catalyst to vary between one-half and one atom of hydrogen per atom of nickel. The activity of the sample was shown to be proportional to its hydrogen content. Surface area decreased linearly with loss of hydrogen until about seventy per cent was removed. If the hydrogen was released rapidly an explosion resulted, probably due to the exothermic recombination of hydrogen atoms. There was no indication that a hydride such as NiH_2 was present in the catalyst.

The study of catalysts, useful in the field of photosynthesis, is a subject of increasing importance. Stephens, Ke & Trivich (68) found cadmium sulfide to be the most efficient of a number of solid catalysts for the photoproduction of hydrogen peroxide. In monochromatic light, it was shown in the cases of cadmium sulfide, cadmium selenide, and zinc oxide that the catalytic efficiencies extend to the absorption limit. A relationship between catalytic efficiency and the crystal structure, semiconducting, and photovoltaic properties of these solids was indicated. It was suggested that these catalytic solids should not be abandoned as devices for capturing solar energy in a form capable of transfer to some chemical system.

Schwab & Goetzeler (69) continued to study the effect of altered magnetic properties of metal and metal alloy catalysts during a catalytic reaction. Ni, Ni—Cr, and Ni—Cu were used as catalysts for the oxygen-hydrogen reaction, the nitrous oxide reduction by hydrogen, and the hydrogenation of ethylene. The reactions were followed for a total temperature change of about 100° across the Curie point. No differences in the energies of activa-

tion were observed between the ferromagnetic and the paramagnetic ranges. Frequently an irregularity in the reaction velocity was observed at the point of magnetic change. This effect was noted more often when temperatures were falling across the Curie point but occasionally it was noted for rising temperatures. One would conclude that the magnetic state of these catalysts had little effect on the catalytic reactions.

Additional excellent papers on the determination of adsorption isotherms and related calorimetric work have appeared. They have filled in details of the total picture of adsorption without adding anything very new or startling. As reported here the developments in the theories of adsorption have been significant.

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MOLECULAR ELECTRONIC SPECTROSCOPY[1,2]

By M. Kasha and S. P. McGlynn

Department of Chemistry, Florida State University, Tallahassee, Florida

This review covers selected topics of research published in molecular electronic spectroscopy in 1955. The topics in this general category which are undergoing rapid development at present are (*a*) spectra of molecular complexes, (*b*) spectroscopy of molecules in crystals, including polarizations and assignments, (*c*) study of spin-intercombinations in molecules, (*d*) study of transitions of n, π type, (e) intermolecular energy transfer; and, extending the general category, (*f*) spectra of transition metal ions in various environments.

From this broad range of topics this review will abstract but one: we shall review the topic "Spin-Intercombinations in Molecules."

Our method will be the setting of a perspective by a coverage of key papers on this topic from past literature. Integrated with this treatment will be all pertinent papers published in 1955. This presentation should have the advantage of a certain unity, although at the same time failing to catalog the many papers published in unrelated fields. The yearly service performed by the *Annual Reports of the Chemical Society* (*London*) cannot be overlooked, however, and makes up for the latter deficiency. As the present method of review is extended, most important papers will have been surveyed in a brief cycle of years.

The topic we have selected is greatly in need of review. In the literature of about ten years ago, very little if any mention was made on the subject of spin-orbital interaction in molecules. The number of papers on this and related topics has increased rapidly in recent years, to the point where they now number well over one hundred. It thus appears worthwhile to organize and examine what has been done thus far in these subjects, and to cast the research of the past year against this background.

SPIN INTERCOMBINATIONS IN MOLECULES

General Background

The full development of this field in research came late in the history of molecular spectroscopy, and in some respects in an unexpected way. The theory of spin-orbital coupling and its application to the electronic spectra of atoms and diatomic molecules had been known since the early years of the

[1] The survey of the literature pertaining to this review was concluded in December, 1955.

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development of quantum mechanics. It seemed natural to suppose with Sponer & Teller (1):

> As in the case of atoms we have, in first approximation, the selection rule that only states of the same multiplicity combine with each other. Intercombinations occur with appreciable intensity only if the molecule contains some heavier atoms.

Developments since 1944 have shown that, although high-Z atoms have their expected effect, frequently spin-intercombinations occur with great intensity even in molecules composed of atoms of atomic number 8 or less. Thus, a type of transition which usually is neglected in atomic spectroscopy except in heavy atom cases, assumes great importance in molecular spectroscopy, and dominating importance in the light-emission properties of most molecules. As we shall see, this extraordinary result is due entirely to the important rôle played by radiationless transitions in complex molecule spectroscopy. As a consequence of these, the lowest triplet states of most molecules are readily populated upon light absorption which excites the allowed singlet states (ground singlet states assumed throughout). On the other hand, the radiative intercombinational transition probabilities are extremely small in (light atom) complex molecules, just as in atomic and diatomic cases. The transition probability for emission of light is measured by the decay constant (reciprocal mean lifetime), so that a high intensity (quantum efficiency) of emission need not be incompatible with a highly forbidden transition.

The fact that complex molecules emit phosphorescence at low temperatures was known since the pre-twentieth-century observations of Wiedemann (2) on solid solutions and Dewar (3) on crystals. The apparent general requirement of a solid state medium was puzzling, if not distasteful to the spectroscopist nurtured on unperturbed gaseous molecule spectra. There were numerous attempts to interpret the spectra on the basis of complicated solid state interactions. Although Lewis, Lipkin & Magel (4) and Terenin (5) speculated on the possibility that the phosphorescence emission might be triplet→singlet in nature, alternative hypotheses were considered equally suitable. Finally, the general identification of the phosphorescence emission of polyatomic or complex molecules as a triplet→singlet emission was made in 1944 by Lewis & Kasha (6). At the time of publication of this paper the theoretical justification for the identification was not very secure, nor was the apparent incompatibility with the behavior of atomic and diatomic systems fully recognized. Nevertheless, the paper catalyzed almost feverish research activity in this field, and it is appropriate to acknowledge a debt of gratitude owed by spectroscopists to G. N. Lewis for his contribution to this general advance in spectral accessibility. Before 1944 the interest in intercombinational transitions in molecules was severely limited by the lack of experimental information.

Subsequently, much work has been published relating to spin-intercombinations: on the triplet→singlet emissions of numerous molecules, the very weak singlet→triplet absorption spectra, the transient triplet→triplet ab-

sorption spectra, the study of spin-orbital perturbations—intramolecular and intermolecular—introduced by high-Z and paramagnetic atoms. These researches have enhanced considerably the understanding of the nature of radiationless transitions in complex molecules, and of the application of spin-orbital coupling theory to molecular cases. Applications are following close on the heels of this spectroscopic work. These include the interpretation of fluorescence quenching, photochemical reactions, photochromism and thermochromism, and perhaps most important of all, the theory of chemical reactivity.

Previous reviews touching on this general topic have been rather fragmentary, but are useful sources: Kasha (7), Förster (8), Kasha (9), and Craig (10).

Theoretical Commentary

Electric dipole and magnetic dipole transitions between pure singlet and pure triplet states are forbidden rigorously on account of the orthogonality of the spin wave-functions. The intervention of spin-orbital coupling brings about a mixing of singlet and triplet states, destroying their purity, and permitting intercombinations between nominal singlet and triplet states to be observed. Great interest attaches, therefore, to the form of the spin-orbital Hamiltonian, since only by a thorough knowledge of its form and action can the spectroscopist realize fully his opportunites for observation of intercombinations.

The spin-orbital interaction operator in its generalized form is given by Dirac (11); [cf. Mott & Sneddon (12)]. The spin-orbital interaction part of the total Hamiltonian is introduced as a relativistic correction. The strongest contribution to spin-orbital interaction occurs when the electron comes closest the nucleus, and is travelling with relativistic velocities. Consequently, insofar as spin-orbital interaction influences chemical behavior (cf. below), it may be said that in those cases there is evidenced a relativistic chemical effect.

How the symmetry of the spin-orbital interaction operator may be deduced for any symmetry of the nuclear potential, V, has been shown by Weissman (13) and Mizushima & Koide (14). However, the simplest discussion is obtained by allowing V to have spherical symmetry, whereupon the properties of the operator become evident immediately. This case is applicable strictly only to atoms [see Kramers (15)], but it has been applied to molecules as an approximation by McClure (16) (*vide infra*). It is found that the spin-orbital interaction operator may be separated into sums containing orbital and spin factors which are separately symmetric or antisymmetric under electron interchange. The antisymmetric spin factors lead to mixing of singlet and triplet states, and the symmetric spin factors lead to multiplet splitting. The orbital factors determine the orbital types of the states which may mix (16, 17). The validity of the separation of the orbital and spin parts of the Hamiltonian has been discussed by Weissman (13) and Ross (18).

The spin-orbital interaction operator involves the gradient of the

potential. This will be largest in the proximity of the nuclei of the atoms on which the (molecular) orbitals are centered, and particularly large close to the nucleus of highest atomic number (Z) in the molecule. In the special case of one high-Z atom in a molecule otherwise composed of low-Z atoms, e.g., thiophene, bromobenzene, etc., where most of the contribution to spin-orbital coupling in a molecular electronic orbital is derived from a single atom, the assumption of a spherical potential as made by McClure (16) is not an unreasonable one. Furthermore, since most of the contribution to the spin-orbital interaction derives from the electron's orbital motion nearest the nucleus, the form of the orbital wave function in this vicinity will be of unusual importance. In ordinary valence and spectroscopic calculations the form of the orbital wave function near the nucleus is comparatively less important. Consequently, the use of Slater-type orbital wave functions in calculations of spin-orbital interaction may be open to question. Both of the published calculations (14, 17) use Slater orbitals.

For a hydrogenic atom, the transition probability for spin-intercombinations has an 8th power dependence (the matrix elements of the spin-orbital interaction depending on the 4th power) on Z, the atomic number [see Condon & Shortley (19)]. A strong Z dependence is found also in molecular spin-intercombinations, as shown in numerous experimental results to be cited below.

In the application of the theory of spin-orbital interaction to the case of benzene, the result is obtained that the observed mean lifetimes for the triplet→singlet emission are up to 1000 times greater than those calculated from the atomic spin-orbital coupling factors [McClure (20)]. McClure (17) has shown that this may arise from a fortuitous cancellation, on symmetry grounds, of the matrix elements for spin-orbital interaction in the planar molecule. On the other hand, Mizushima & Koide (14) have shown that σ-π interaction would be sufficient to account for the observed long intercombinational lifetime in benzene. In order to decide which of the theories is applicable to benzene, polarization studies of the phosphorescence emission would be necessary. Thus far, such a study has not been made.

Photomagnetism Studies

Before proceeding to spectroscopic observations, it is worthwhile to review the experimental work on the paramagnetic susceptibility of the phosphorescent, or lowest triplet, state of complex molecules. At the time that the phosphorescence emission was interpreted as a triplet→singlet emission, such measurements seemed an important and necessary proof of the interpretation. Moreover, here was a delicious opportunity, since near-saturation of the excited state could be obtained under certain conditions [see (4) for example]. Subsequent spectroscopic studies, based on the nature of spin-orbital interactions, have made direct measurements of paramagnetic susceptibility unnecessary for assignment of state multiplicity. Nevertheless, it is an interesting chapter in the development of the field, and new work on this phase has appeared very recently.

Lewis & Calvin (21) carried out exploratory experiments on the paramagnetism of a dyestuff excited to its phosphorescent state. This work was followed by a thorough quantitative study by Lewis, Calvin & Kasha (22). For acid fluorescein dye a satisfactory measurement of the paramagnetic susceptibility was obtained, confirming the triplet assignment for the phosphorescent state.

It is interesting to note that empirical photomagnetic experiments were carried out earlier by Fröhlich, Szalay & Ször (23). These authors investigated the behavior of dyestuffs in solid solutions, in the form of plates, suspended in a magnetic field. A photomagnetic effect was noted. Yamamoto (24) also carried out a series of magnetic dichroism researches on solid solutions of dyestuffs, upon illumination. His results confirm the photomagnetism results of Lewis, Calvin & Kasha (22).

Porter (25) has commented on the need for further paramagnetism studies of the phosphorescent state; he was unaware of the researches described immediately above.

Direct measurements of paramagnetic susceptibility have been extended by Evans (26) recently to include fluorescein dye, 1-hydroxy-2-naphthoic acid, and triphenylene. Using an apparatus different from the Theorell balance used by Lewis, Calvin & Kasha (22), Evans not only observed positive results in each case, but also was able to follow the decay of paramagnetic susceptibility with time upon extinction of the exciting light. The time constants for this decay, which was observed to be exponential, coincided with the decay constants for the phosphorescence emission. This provides proof that the paramagnetism arises from excited triplet states which decay spontaneously, and not, e.g., from radicals disappearing by a bimolecular recombination process.

Radiationless Transitions: Intersystem Crossing

In molecular electronic spectroscopy "internal conversion" may be defined as the rapid radiationless combination of electronic states of like multiplicity. Experience indicates that, in general, internal conversion takes place between excited levels, but not between the lowest excited level and the ground level. This evidence is summarized in the rule (9): The emitting level of a given multiplicity is the lowest excited level of that multiplicity. This behavior depends on the relative spacing of the electronic levels, and on the necessity for removal of the excess vibrational energy by intermolecular collisions. In solid solution experiments at 77°K. only the behavior of naphthacene (27) and azulene (28) have provided anomalies, both of these also having exceptional energy spacings. Theoretical studies relating to the general problem of radiationless transitions in molecules have been carried out by Teller (29), Duschinsky (30), and Davydov (31).

Recently, crystal spectroscopic studies at 20° and 4°K. have provided many further examples of the breakdown of normal internal conversion. These examples are particularly interesting since they involve molecules which behave normally at 77°K. in solid solution emission studies. Evi-

dently, at very low temperatures, the intermolecular collision process is inhibited to the point where vibrational energy cannot be carried off effectively. Hence, essentially "resonance" emission may occur. This technique is rich in possibilities for resolution of superposed electronic transitions in molecules. Such observations have been reported recently in a series of exploratory researches on molecular crystals by Pesteil *et al.* (32 to 39). Of particular interest is their report of two triplet→singlet emissions in benzene: one at 30574 cm^{-1}, which they assign as ${}^3B_{1u}\rightarrow{}^1A_{1g}$; and one at 38724 cm^{-1}, which they assign as ${}^3E_u^-\rightarrow{}^1A_{1g}$. The lowest triplet of benzene is well known from earlier work (6, 40, 41, 54, 55). The second triplet has been predicted by theory [see Roothaan and Mulliken (42)] and it has been reported by Pesteil to be evident in absorption in the spectrum of crystalline benzene at 83°K. (43, 44) [see footnote on p. 230, ref. (10), however]. The observations of Ham (45), which were described as evidence for the second triplet in benzene, have been criticized by Bayliss & Hulme (46). Further examples of the apparent breakdown of internal conversion have been found recently by Sidman & McClure (47) in their very thorough study of the absorption and emission spectra of solid crystal solutions biacetyl and biacetyl-d-6 at 20°K. and 4°K.

A further anomaly of low temperature crystal spectroscopy was noted by Pesteil *et al.* (see above), in which apparently at the lowest temperatures, the electronic transition is displaced to lower frequencies by a vibrational quantum, compared with higher temperature spectra. We shall not elaborate on this since it has no direct bearing on internal conversion.

"Intersystem crossing" has been defined as the spin-orbital coupling dependent internal conversion in molecules (9). The intensity of the phosphorescence emission (in terms of quantum efficiency, i.e., number of T→S quanta emitted per number of S′←S quanta absorbed) does not measure the probability of T→S emission, but is determined by the ratio of the transition probabilities for the (radiationless) intersystem crossing (S′→T) and the spontaneous fluorescence (S′→S). (It is assumed here that S′ is an excited singlet state lying above the lowest triplet state T, and that most of the triplet excitation occurs by intersystem crossing from this singlet.) The intersystem crossing ratio $\chi=\Phi_P/\Phi_F$ therefore measures this transition probability ratio [Kasha (9); see McClure (20), especially Table VII], and states the relative quantum efficiency for phosphorescence and fluorescence. If the transition probability for fluorescence becomes too small, the lowest triplet state may become the only emitting state in the molecule. This situation is especially common where the lowest singlet-singlet transition is of n, π type (9).

Since intersystem crossing is spin-orbital coupling dependent, perturbation effects involving the electric field of high-Z nuclei or the magnetic field of paramagnetic atoms should be observable. Kasha (9) has observed a strong Z dependence of the Φ_P/Φ_F ratio in halogenated aromatic molecules [cf. Yuster & Weissman (48)]. In certain organometallic chelates involving rare earth

ions, Yuster & Weissman (48) have found the same effect, and in a case where the ion was paramagnetic, an especially strong perturbation was noted. In all such studies the main effect observed is a great increase in the Φ_P/Φ_F ratio, while the total quantum efficiency remains essentially constant.

Recently Becker & Kasha (49, 50) have made use of spin-orbital perturbation effects to establish the lowest triplet state of the chlorophyll molecule. A porphyrin molecule, phthallocyanine, and several cholorphyll species were studied each without a metallic atom, and containing both heavy and paramagnetic atoms. The effects observed were exactly parallel to the predictions of spin-orbital coupling theory. The lowest triplet levels of the chlorophylls and the porphyrin studied were thus established with certainty.

Porter & Windsor (51) [see also Porter (25)] have applied the synchronized flash (flash photolysis) spectroscopic method to the study of triplet states in fluid solutions. Their kinetic analysis has given important new information concerning the intersystem crossings involved. However, at the same time, further problems of interpretation have arisen, causing these authors to emphasize the need for a critical examination of the triplet state interpretation on the phosphorescent state. At this juncture, there seems to be no doubt concerning the validity of the triplet state interpretation. However, the flash technique undoubtedly offers a valuable method of study of triplet state excitations, depopulations, and reactions.

Triplet States: Triplet→Singlet Emission Studies

Lewis & Kasha (6) gave spectroscopic data on the phosphorescence emission spectra of 89 molecules. We have already discussed their interpretation of these as lowest triplet→singlet emissions (see General Background section). Of the molecules studied, only the results given for stilbene and ethylene and its halogen derivatives are now known to be wrong (see Potts, in section on Singlet→Triplet Absorption Spectra); for the remaining cases the emissions are authentic. Kasha (7) presented a discussion of the function of the rigid glass solution, and elaborated on the mechanism of excitation of the lowest triplet state; further triplet→singlet emission data were reported (e.g., hexachlorobenzene and phenanthrene). One general conclusion drawn from this earlier work is that the viscous or rigid medium used as a solvent serves mainly to inhibit diffusion controlled quenching of the triplet state. On the other hand, Lewis & Kasha (52) stressed the fact that if the lowest triplet state intrinsic mean lifetime were short enough, triplet→singlet emission would be observable even in the liquid and gaseous state. Porter & Windsor (51) in the papers already referred to have made studies recently on the lowest triplet state in liquid solutions (see Radiationless Transition section above, and section on Triplet→Triplet Absorption Spectra, below), although under their conditions triplet→singlet emissions could not be observed directly. The studies of luminescence spectra of vapors, by Robinson (53), involve triplet→singlet emissions. The case of biacetyl vapor luminescence is another well known example (52; see also 47) of

a strong triplet→singlet emission of a complex molecule in the vapor state. In such cases, the inherent short lifetime allows emission to occur without complete quenching. In other cases, where the triplet→singlet lifetime is relatively long (see below), only singlet→singlet emission is observed in the vapor luminescence spectrum.

More detailed studies of triplet→singlet emission spectra have been made subsequent to the research of Lewis & Kasha. Thus, the triplet→singlet emission spectrum of benzene was carefully re-studied and a vibrational analysis carried out by Shull (40); parallel studies on benzene have been made by Dikun & Sveshnikov (41, 54, 55). Pesteil *et al.* (33, 39) have recently studied the triplet→singlet emission in crystalline benzene, and also crystalline hexachlorobenzene (37, 38), at very low temperatures. Some of their results already have been mentioned in the section on Radiationless Transitions. The naphthalene triplet→singlet emission was restudied by Ferguson, Iredale & Taylor (56), who gave vibrational analyses for naphthalene, and monosubstituted and disubstituted naphthalenes. In the case of anthracene, Reid (57) presented indirect evidence against the lowest triplet level reported by Lewis & Kasha (6). Padhye, McGlynn & Kasha (58) have restudied the lowest triplet level in anthracene and have confirmed the level reported by Lewis and Kasha. Triplet→singlet emission spectra of anthracene and several substituted anthracenes, singlet→triplet absorption spectra, and solvent-perturbation experiments (see below) were used to confirm the assignment. McGlynn, Padhye & Kasha (59) presented a correlation diagram for the lowest triplet levels for the first four linear polyacenes. Craig (10) has discussed the symmetry assignment of electronic levels in this series.

Besides the polyacene hydrocarbons described above, phosphorescence spectra were reported for various pyrene hydrocarbons by Ilina & Shpolskii (60) and for coronene and 1,2-benzoperylene by Bowen & Brocklehurst (61). McClure (20) had previously reported frequency data on triplet→singlet transitions of pyrene, coronene and other hydrocarbons not studied by Lewis and Kasha. Neporent & Inyushin (62) reported phosphorescence and fluorescence spectra of phthallimide and eleven derivatives.

Becker & Kasha (50) published spectroscopic data on the lowest triplet→singlet transitions in several chlorophylls and porphyrins. Their observations are complemented by the studies of Livingston (6), who has used the synchronized flash technique to study the lowest triplet state of the chlorophylls. The observations using this technique yield triplet→triplet absorption spectra, and also lifetimes of the triplet state under the experimental conditions used. The research of Witt (64) parallels that of Livingston.

The transition probability for triplet→singlet emission is measured by the decay constant, or the reciprocal of the intrinsic mean lifetime. Numerous studies of the mean lifetime of the lowest triplet state of molecules are now published. Some discretion must be exercised in using the published data directly, since only the intrinsic mean lifetime in the absence of quenching is

a true measure of the transition probability. Probably, lifetimes determined for dilute solutions of a molecule in rigid glass solvents approach the intrinsic lifetimes, according to quantum efficiency measurements (see below). McClure (20) published the first detailed study of triplet→singlet lifetimes in complex molecules. His measurements provided proof of the intercombinational character of the emission, through his demonstration of the Z-effect on the emission lifetime in halogenated hydrocarbons. His correlation of the mean lifetimes with spin-orbital coupling factors for the substituting atoms gave semi-quantitative agreement. Similar observations were made by Yuster & Weissman (48) on the dibenzoylmethane derivatives of trivalent metal ions, including some rare earth ions. Kaskan & Duncan (65) made a study of the triplet→singlet emission lifetimes of ketones in the gaseous state. An empirical study of phosphorescence lifetimes was made by Sveshnikov & Petrov (66), who studied the influence of the medium on the lifetimes. A comprehensive empirical study of phosphorescence lifetimes was published by Dikun, Petrov, & Sveshnikov (67), with data on numerous mono, di, and trisubstituted hydrocarbons. Similar empirical phosphorescence lifetime studies were made by Pyatnitskii (68). The study of triplet→triplet absorption spectra (see pertinent section, following) affords independent information on lowest triplet state lifetimes, although in fluid solvents the quenching effect markedly shortens the observed lifetime. Thus, Craig & Ross (69), Porter & Windsor (51), Livingston (63) and Porter & Wright (70) have determined lifetimes by following the decay of triplet→triplet absorption. Apparatus for phosphorescence lifetime determination has been described recently by Skarsvag (71) and van Roggen & Vroom (72).

Studies of quenching of phosphorescence of organic molecules have been published recently by Kato & Koizumi (73) and Kato, Kimura & Koizumi (74). Measurements of absolute yield of phosphorescence were reported earlier by Gilmore, Gibson & McClure (75).

In this paragraph we shall itemize theoretical papers having special reference to intercombinations and triplet states in molecules; papers on calculation of electronic levels in which triplet states are incidental will not be covered. In the section Theoretical Commentary reference has already been made to the paper on selection rules for intercombinations by McClure (16) and the paper on the vector model for spin-orbital interaction by Weissman (13). The papers on calculation of matrix elements for spin-orbital coupling in benzene by McClure (17) and Mizushima & Koide (14) also were alluded to briefly. Transition probability calculations for spin-orbital interaction in atoms had been published by King & Van Vleck (76). Barnes, Bray & Harrick (77) reported briefly on spin-orbital and spin-spin interaction parameters for molecular hydrogen, as derived from radiofrequency spectroscopic measurements. Herman (78) considered symmetry selection rules involved in molecular intercombinations. This paper seems to suffer from inaccurate translation and is otherwise difficult to evaluate. Kovner & Sverdlov (79) have described a simple method for calculation of triplet states

by the Valence Bond method (Rümer diagrams). Longuet-Higgins & Pople (80) have studied excited states of odd alternant hydrocarbon radicals and ions, and relate the singlet-triplet separation of the ion to the separation of the two low-lying doublets of the radical [cf. Longuet-Higgins & Murrell (81)]. Merrifield (82) has compared matrix elements for excitons of singlet and triplet multiplicity.

Singlet→Triplet Absorption Spectra

Radiative spin-intercombinations are highly forbidden in complex molecules just as in the case of atoms. Consequently, singlet→triplet absorption intensities are extremely low, and triplet→singlet emission lifetimes correspondingly long. A factor of about 10^6 relates the corresponding singlet→singlet transition probabilities.

Because of the very low transition probabilities for the spin-intercombination absorption case, considerable difficulty is experienced in observing singlet→triplet electronic absorption bands, and distinguishing them from bands due to vibrational harmonics and impurities. This will be evident in the examples which follow.

Lewis & Kasha (52) carried out the first systematic search for singlet→triplet absorption bands in molecules. They made use of the classical relation between absorption and emission probabilities [cf. references in Kasha (9)] as a guide to amenable cases. Their work suffered from their failure to realize the importance of the Z-effect on intercombinational transition probabilities. Consequently, only the singlet→triplet absorption band reported for benzene is authentic; the absorption bands for the remaining molecules investigated by them have been shown subsequently to be singlet →singlet in nature. McClure, Blake & Hanst (83) made use of the Z-effect in intercombinations in their study of singlet→triplet absorption bands of halogenated benzenes and naphthalenes.

The case of benzene deserves special mention as the singlet→triplet absorption band has been investigated by numerous researchers. Sklar (84) first reported observing this band, although the absorption curve was not published. Lewis & Kasha (52) reported a detailed spectrum observed for 10 cm. of liquid benzene. The correspondence with the previously observed triplet→singlet emission was used as a criterion of authenticity. Also they demonstrated that the vibrational overtones, although observable even in the visible region, could not account for the observed ultraviolet bands owing to the rapid diminution of the intensity of overtones with frequency. Pitts (85) reinvestigated the same band. McClure, Blake & Hanst (83) gave additional proof of its intercombinational character by demonstrating its intensification with increasing Z of substituent atoms. Shibata, Kushida & Mori (86), on the other hand, reported weak absorption bands for benzene in the visible region. They designated these as singlet→triplet, whereas they were identified previously by Lewis & Kasha (52) as merely vibrational harmonics [See reference (10), footnote on p. 230; and reference (59), footnote 12]. Cheshko (87) believed the bands reported for benzene by

Lewis & Kasha (52) to be due to impurities; however, the data he published on his research merely indicates that his benzene was never pure enough to observe the bands.

In the case of pyridine, Reid (88) reported in detail on two weak transitions in the ultraviolet region. Recently Brealey (89) has shown that both of these bands are due to a very small impurity of pyrazine in pyridine.

In the ethylene molecule Snow & Allsopp (90) made an early report on a weak absorption band near 2100 A, which they assigned as singlet→triplet. Moffitt (91) supported their assignment with theoretical calculations. Thus, this assignment of Snow and Allsopp is evidently the first authenticated singlet→triplet observation in complex molecules. These bands were studied further by Carr & Stücklen (92), Picket, Muntz & McPherson (93), and recently by Potts (94). Lewis & Kasha (6) had reported phosphorescence emission in halogenated ethylenes near 4000 A. Potts searched for phosphorescence in tetramethylethylene and found none. From the energy and the lifetime point of view, the phosphorescences reported by Lewis and Kasha for ethylenes do not appear to be authentic.

Sidman & McClure (47) have recently observed weak absorption bands in biacetyl at low temperature, which they asign as the lowest singlet→triplet absorption. Padhye & Desai (104) have reported on the lowest singlet →triplet absorption band in thiophene.

The difficulties which occur in the discrimination of very weak absorption bands due to impurities and vibrational harmonics, from those due to authentic spin-intercombinations can be overcome in applicable cases by the use of the solvent-perturbation technique [Kasha (95); see section on Intermolecular Spin-Orbital Perturbations].

Triplet→Triplet Absorption Spectra

Triplet→triplet absorption bands are of course not intercombinational in nature, but are discussed here because of their dependence on triplet excitation. The bands are inherently medium strong to intense, since the only selection rule would involve orbital symmetry. Where favorable population of the lowest triplet is attainable, the transient absorption originating in this metastable state is readily observed.

Early in the research conducted by Lewis on the phosphorescence state of molecules, observations on transient absorption spectra were recorded and identified as "absorption spectra of the phosphorescent state." Today these are recognized as triplet→triplet absorption spectra, and are essential for the location of upper triplet levels in molecules.

Lewis, Lipkin & Magel (4) published data on a triplet→triplet absorption band of the acid fluorescein dye, and Lewis & Lipkin (96) observed a triplet→triplet absorption band in diphenylamine. Clar (97) reported observations on a triplet→triplet absorption band in triphenylene. Sveshnikov & Dikun (98) reported difficulty in reproducing Lewis, Lipkin & Magel's result on acid fluorescein.

McClure (99) made a general study of triplet→triplet absorption spectra

in complex molecules. Spectra and frequencies were reported for ten molecules, mainly aromatic hydrocarbons and simple derivatives. Craig & Ross (69) extended triplet→triplet absorption studies still further, giving data on various aromatic hydrocarbons and multiple ring nitrogen heterocyclics. Their determination of lowest triplet state lifetimes have been referred to previously. Craig and Ross also noted photodecomposition effects, which constitute an interference in the physical absorption work.

All of the above observations have been made in rigid glass solutions at low temperature. The development of the synchronized flash spectroscopic method has made it possible to study triplet→triplet absorption spectra in fluid solutions at room temperature. Thus Porter & Windsor (51), Porter & Wright (70), Livingston (63), and Witt (64) have carried out such studies in papers already referred to. McClure & Hanst (100) have recently used the sychronized flash technique to study triplet→triplet absorption in aromatic ketones.

Ross (101) has made a theoretical study of the optimal optical conditions for triplet→triplet absorption studies.

There are two difficulties which exist in this field at present. First, photodecomposition may constitute a serious interference especially in the flash method, owing to the high light intensities used. Second, there is a gap at present, due to experimental inaccessibility, between the lowest triplet observed in phosphorescence, and upper triplets observed in triplet→triplet absorption. Thus, in benzene, no triplet→triplet absorptions have been observed as yet, possibly because they exist in the near infrared region.

The observations of thermochromism are related to the subject of triplet→triplet absorption spectroscopy. These are discussed in the last section of this review.

Intermolecular Spin-Orbital Perturbations

Even if only intramolecular spin-orbital effects could be observed, intercombinations in molecules would have an important bearing on chemical problems. The discovery of intermolecular spin-orbital perturbations serves to make ideas on intercombinations in molecules of direct applicability to the development of chemical reaction mechanisms. Such a possibility is just becoming apparent to chemists and has been almost entirely neglected up until now. In this section we shall be concerned with physical intermolecular effects. Chemical effects will be listed in the next section.

Kasha (95) made use of the Z-effect on intercombination absorption intensity, extending previous work in an intermolecular spin-orbital perturbation experiment. Ethyl iodide was used as a solvent to bring about an enhancement of the singlet→triplet absorption intensity in a naphthalene derivative. Ham (45) made similar observations on benzene, in which he observed enhancement of absorption bands in between the individual singlet→singlet near ultraviolet absorption bands of benzene. Bayliss & Hulme (46) have questioned Ham's assignment of the observed bands as

singlet→triplet; admittedly his observed intensities are very high for intercombinations, and the possibility of confusion with the singlet→singlet absorptions in this case is rather great.

McGlynn & Kasha (102) have made a comprehensive extension of the earlier observations of Kasha (95). Many new examples were found of singlet→triplet band enhancement, and the dependence on Z was fully delineated. Up to one hundred-fold enhancements were observed with alkyl iodide solvents. Of particular interest is their demonstration that vibrational harmonics and impurity absorption bands (which are necessarily singlet→singlet) are unaffected by solvents containing high-Z atoms. This, as mentioned earlier, offers a criterion of authenticity for singlet→triplet absorption work, in those cases where the solvent-perturbation method can be used. In some cases, a reaction of the solute with the high-Z atom solvent makes the method inapplicable. Dyck & McClure (103) have recently used the solvent-perturbation method to induce the singlet→triplet absorption band in trans-stilbene. This band could not be detected in the absence of an external perturbation, and the converse emission also was not observable.

The solvent-perturbation experiments of Kasha (95) were undertaken because of the known Z-dependence of intermolecular fluorescence quenching. Since the spin-orbital Hamiltonian has a high Z-dependence, it was expected that the mechanism of "heavy atom" fluorescence quenching could be due to an intermolecular spin-orbital perturbation. The demonstration of singlet→triplet absorption band enhancement offered direct proof of this interpretation of fluorescence quenching. This paved the way to other intermolecular or chemical applications.

The Russian researchers have thought along rather different lines from those described in this review. The work of Terenin, Karyakin *et al.* indicate that they have not recognized the mode of excitation of triplet states, and the dependence of spin-orbital interaction on atomic number. Thus, Ermolaev & Terenin (105) do not believe that triplet states can be excited directly by light absorption and dispute the Lewis & Kasha (6) interpretation of phosphorescence. They believe that intermolecular energy transfer may be required for excitation of triplet→singlet emission. Terenin (5) in his first writings on the subject acknowledged Lewis, Lipkin & Magel's (4) tentative discussion on the possibility of the triplet→singlet interpretation of phosphorescence. On the other hand, in this and later papers he and his coworkers laid emphasis on the need for "paramagnetic quenching" as a mechanism of excitation of the lowest triplet state. In a long series of researches Terenin and Karyakin studied the intermolecular paramagnetic quenching by O_2 molecules (106–110) and NO molecules (111). Mainly anthraquinone derivatives were studied, both in the gaseous and in the adsorbed state. Karyakin & Kalenichenko (112) continued their efforts to induce triplet→singlet emission by intermolecular magnetic perturbation effects by adsorption of aminoanthraquinones on silica gel surfaces impregnated with paramagnetic ions, Cu^{++}. They observed an infrared lumines-

cence which they believed to represent the triplet→singlet emission of the adsorbed molecule. Probably they had observed an intramolecular energy transfer between the π-electron levels of the aminoanthraquinones and the d-levels of the Cu^{++} ion; the reported emission was at 8800 A, which corresponds to the wavelength of the cupric absorption band. Such intramolecular energy transfers are known since the work of Weissman (113) on rare earth chelates; in the experiments of Karyakin and Kalenichenko adsorption probably is accompanied by chelations of the metal by the organic molecule adsorbed.

Bowen and co-workers also have carried out intermolecular quenching experiments, investigating fluorescence quenching in the gaseous state by both high-Z atom containing molecules, and paramagnetic molecules. Bowen & Metcalf (114) and Metcalf (115) reported preliminary studies of this sort, following earlier work by Bowen *et al.* Recently Stevens (116) has adduced a spin-orbital perturbation mechanism to explain high-Z and paramagnetic atom quenching. Bowen (117) and Bowen & West (118) have reported further work on fluorescence quenching, with intercombinational interpretations.

Reid (57, 119) and Moodie & Reid (120) have investigated the light emission properties of both trinitrobenzene-aromatic hydrocarbon molecular complexes, as well as hydrocarbon-hydrocarbon complexes. The trinitrobenzene-aromatic hydrocarbon complexes yielded emission spectra closely resembling the triplet→singlet emission spectra of the parent aromatic hydrocarbon. Reid has proposed a mechanism to account for this behavior based on the idea that in the molecular complex the plane of symmetry of the hydrocarbons is destroyed, resulting in non-vanishing matrix elements for spin-orbital interaction as compared with the parent hydrocarbon. Orgel (121) and Sponer (122) have discussed some aspects of this work. The results of Reid *et al.* are especially interesting since they illustrate that in aromatic hydrocarbons the intercombinational transition probability is sensitive to other effects than those due to field of high-Z and paramagnetic atoms.

Intercombinations in Photochemical and Chemical Reaction Mechanisms

As an empirical science, photochemistry has been a field of active investigation paralleling the earliest investigations of spectroscopy. The application of spectroscopic theory to photochemistry has been fragmentary. Probably, the neglect of intersystem crossing information in photochemical researches has resulted in a delay in spectroscopic interpretation. Typifying some of the more recent photochemical investigations has been an emphasis on the role of triplet states and intercombinations in photochemical processes. In an earlier paper Calvin & Dorough (123) discussed a photooxidation reaction with a possible triplet state intermediate. Recently, Seely & Calvin (124) have studied in detail a photoreduction reaction involving a triplet state

intermediate. These researches deal with porphyrin-like molecules. Ashkinazi & Karpitskaya (125) have described photochemical investigations on Zn and Cu analogs of cholorophyll. Becker & Kasha (49, 50) have discussed the role of triplet states in the photosynthetic system. Beacom (126) has investigated photochemical reactions of transition metal complexes.

Bowen & Tanner (127) have published recent results on the photochemistry of anthracene. Livingston (128) has reviewed the primary act in photochemical reactions sensitized by polyatomic molecules. Fujimori (129) has described a comprehensive photochemical investigation which reviews general interpretations in various systems of biological importance, including photosynthesis. Norrish & Porter (130) discussed the production of triplet state molecules by photolytic techniques. Callear & Robb (131) described work on the mercury photosensitized decomposition of ethylene, in which the lowest triplet state of ethylene is described as an intermediate in its decomposition to acetylene and hydrogen. A valuable discussion of this process was conducted by Bauer *et al.* (132).

In chemical reaction theory, triplet states usually are not involved directly in thermally induced reactions, although there are some cases in which a particularly low energy barrier makes this possible. A situation of this sort prevails in the recent researches on relative methyl affinity (relative rate of addition of methyl radicals) by Szwarc *et al.* (133–137). This work indicates that there is a linear relationship between the log of the methyl affinity and the energy of the lowest triplet state of the aromatic molecule, for some 14 aromatic hydrocarbons investigated. The transition state is taken to lie at the position of crossing of the two energy curves which apply to the interaction of the radical with the singlet ground state and the lowest triplet state. The experimental methyl affinity values of Szwarc *et al.* have been corroborated by Hey & Williams (138), and Coulson (139) showed how theoretical values may be deduced. Levy, Newman & Szwarc (137) have referred to unpublished work of Coulson and of Matsen which indicates that the correlation proposed by Szwarc *et al.* may not be unique.

Isomerization reactions involving triplet state mechanisms have been studied quite extensively in the past, e.g., in the work of Magee, Shand, & Eyring (140). Recently Davies & Evans (141) have extended this field of research.

Magnetic catalysis of chemical reactions has been considered in many early researches, and we include a brief review here for its relation to the present problem. A theoretical study of the mode of interaction involved has been published by Wigner (142). An early research in this topic was published by Harman & Eyring (143), who considered the effect of paramagnetic substances on chemical reactions. Gelles & Pitzer (144, 145, 146) have studied the effect of diamagnetic and paramagnetic ions of the same size and charge on decarboxylation rates of malonic type acids. The paramagnetic ion Dy^{+++} yielded a 10 per cent increase in rate of the reaction at the conditions used.

A cis-trans isomerization is involved in the proposed reaction mechanism. McConnell (147) has proposed an alternative interpretation to the magnetic interaction ideas favored by earlier workers.

Thermochromism and Photochromism

Recent researches on thermochromic and photochromic phenomena, i.e., the reversible production of colored substances upon heating and light excitation, have indicated some interesting relationships to the spectroscopic work reviewed above. On the other hand, the additional complexity of these topics has left their interpretation in a rather uncongealed state for the present.

Schönberg & Schutz (148) in an early paper reported on the thermochromism of bixanthylene. Recent researches by Schönberg *et al.* (149, 150) and Mustafa & Sobhy (151) have resulted in the conclusion that substituents which hinder coplanarity of the two main parts of the molecule lead to an interference with thermochromic behavior. Grubb & Kistiakowsky (152) studied the thermochromism of bianthrones. Their interpretation indicates that the origin of color is due essentially to a triplet→triplet absorption, in which the lowest triplet is populated by thermal excitation from the ground singlet. Matlow (153) carried out an LCAO-MO calculation on bixanthylene and bianthrone, giving values of the energy differences between the singlet planar ground state molecule and the lowest triplet state perpendicular molecule; these results are in accord with the experimentally observed values. Nilsen & Fraenkel (154) carried out paramagnetic resonance absorption experiments on bianthrone, which serve to confirm the existence of paramagnetic molecules in solution, whose concentration is temperature dependent. At room temperatures it was found that the paramagnetic molecules were absent. In the solution experiments, the paramagnetic resonance absorption was reversible with temperature. In the crystalline state, an irreversible high temperature paramagnetic resonance absorption was noted.

Photochromic behavior has been reported by Hirshberg (155) in compounds related to bianthrone. The color is induced by ultraviolet illumination at low temperatures, and is spontaneously reversible in the dark at a rate depending on the temperature. Presumably, the colored species is not a product of photofragmentation, but is some electronic state or geometrical modification of the original molecule. The relation of this modification to that produced in thermochromism studies has become a topic of some controversy. Careful spectroscopic investigation should eventually decide the issue. In this section we omit all discussion of photochromism in which definite evidence of photofragmentation has been found, as in the work of Lewis & Lipkin (96) and other well known papers by Lewis. Bergmann & Fischer (156) and Hirshberg & Fischer (157) reported on thermochromism and photochromism of bianthrone compounds, and Hirshberg & Fischer (158) reported similar results in spiran compounds. Kortüm, Theilacker *et al.*

(159, 160) have taken issue with the interpretation made by Hirshberg and Fischer regarding the relation between the photochromic and thermochromic phenomena. Unfortunately, a somewhat mediaeval polemic has marred the discussion of this subject (161, 162).

The study of photochromism and thermochromism should be of exceptional interest to the spectroscopist because of the possibilities it offers for the study of low-lying electronic states of complex molecules. Extrapolating the paramagnetic resonance absorption results of Nilsen & Fraenkel (154) indicates these could be exceptionally low-lying triplet states. The results reported also indicate a pronounced effect of the solid medium on the potential function of rather cumbersome molecules, apparently hindering the free excitation of electronic states of contrasting geometry. It is quite possible that the full understanding of thermochromic and photochromic phenomena in appropriate complex molecules could serve as the shortest bridge between molecular spectroscopy and molecular chemistry.

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VIBRATION-ROTATION SPECTROSCOPY[1]

By Ralph S. Halford and Isao Ichishima[2]

Department of Chemistry, Columbia University, New York, New York

Approximately four hundred titles pertaining to the topic of vibration-rotation spectra appeared during the calendar year 1955 among the contents of the forty-three periodicals that we attempted to survey. Merely to list this bibliography without comment, in the conventional style, would consume more than half of the printed pages assigned to this article.

We are thankful as we contemplate the accelerating growth in the annual volume of literature that our invitation to serve as reviewers arrived when it did, rather than a decade later.

We are inclined at the same time to doubt that many of our readers, especially ones who busy themselves with adding to reviewers' tasks, could literally appraise critically the often highly technical contents of current contributions at an average rate exceeding one per day throughout an entire year. We shall not pretend that we could do so.

Such is one facet of the present status of our subject. The commentary doubtless applies as well to the present status of science in general.

We must be content with reporting some impressions. We realize that these will mirror the eccentricities of our own approach to and interest in the topic of vibration-rotation spectroscopy.

Fortunately, from the standpoint of one seeking to keep abreast of the rising tide of literature it is still possible to form rapidly some fairly accurate and detailed impressions of current developments. Conveniently, about forty per cent of all pertinent contributions appear in one periodical—*The Journal of Chemical Physics*—while about eighty per cent can be found in a list of ten widely circulated periodicals, all in the English language.

The bulk of current contributions fall into one or another of several well established, by now almost stereotyped patterns. Each pattern has its own special motivation in the conceptual realm, its standard plan and techniques of observation, its characteristic theoretical machinery, and leads automatically to its own particular package of conclusions. New substances are fed continuously into these data-production lines, new numbers come out.

In short, a large proportion of current effort can be called programmatic. To do so is not to disparage it. The very existences of these programs, the vigor with which they are pursued, the demand for the volumes of their outputs, all testify to their significances. We urge the unacquainted reader to become familiar with them. The findings of these programs play an essential

[1] The literature survey in preparation for this article was concluded in mid-January, 1956 and covered, insofar as possible, the entire calendar year of 1955.

[2] Assistant Professor, Department of Chemistry, Tokyo University, on leave of absence 1954–56. Boese Postdoctoral Fellow at Columbia University 1954–55.

role in the conceptual schemes employed by virtually every branch of chemistry. Programmatic research is the bone and muscle of vibration-rotation spectroscopy.

We shall dwell only briefly upon the current programmatic contributions, nevertheless, in the course of this review, except where these seem to us to foretell of new varieties or muchly refined morsels of knowledge. For the benefit of any newcomers to our subject we shall include a brief allusion to each of the major programs along with reference to some recent book where the particular program is illuminated at more appropriate length.

When the current programmatic contributions are subtracted from the total of recent literature the residue contains a fund of explorations and novel or controversial findings that is manageable within the limitations imposed upon this review.

The contest for knowledge that is waged with the weapons of vibration-rotation spectroscopy can be looked upon equally well from many points of view. From our points of view the contest is fought in the conceptual realm, over the territory of molecules. We see within this territory two principal arenas: an *intramolecular* one where the contest is of longer standing and an *intermolecular* one into which it has been flowing recently with great vigor.

The intramolecular arena is concerned primarily with measurements and interpretations of modal frequencies. A substantial fund of empirical knowledge indicates that modal frequencies of intramolecular origin are perturbed almost negligibly relative to usual observational accuracy by molecular interactions. Extrapolated magnitudes for absolute intensities, obtained as limits approached by series of appropriate observations upon absorption by a vapor, belong also to the intramolecular arena.

The intermolecular arena is entered through observations upon line shapes or band contours (the latter including for convenience the merely qualitative observation of multiplet structure in vibration spectra of crystals) and upon intensities, but only to a very limited and often negligible degree by measurements of frequencies. There is one notable exception to this generalization: a gross frequency displacement caused by hydrogen bonding.

The Intramolecular Arena

Pure rotation spectra are observed programmatically with gases in the microwave region of the spectrum. Frequencies absorbed are measured with a standard kind of spectrometer to within parts per million. If the substance was chosen judiciously, molecular moments of inertia can be computed from the observations. With observations for several isotopic species, variations in the moments of inertia can be used to discover the molecular architecture, expressed in terms of equilibrium bond distances and bond angles. When some of the constituent nuclei possess quadrupole moments the observed spectra may exhibit fine structure of a corresponding kind. Observations upon this fine structure are attributed to properties of the electron probability distri-

bution in the immediate vicinity of a quadrupolar nucleus and interpreted further in the vernacular of valence theory. With a superabundance of data suitable for architectural characterization isotopic mass ratios might be reported.

Microwave spectra are rather complicated and the interpretation becomes at times quite intricate. Properties of molecular models that seem esoteric from the standpoint of a physical chemist must be treated as a matter of course because of the superlative accuracy and extreme resolution that can be achieved in the measurement of microwave frequencies. Fortunately there are now two books, one by Gordy, Smith & Trambarulo (1), another more recent one by Townes & Schawlow (2), to dispel the mysteries.

Microwave spectroscopy is comparatively a new weapon but in its short lifetime it has become already a potent provider of information pertaining to molecular architecture. The current literature contains a number of excellent examples of skillful investigations and we regret that we lack the space to enumerate them. Two, one concerning methanol and the other methyl mercaptan, will be cited presently in another connection.

When molecules can execute hindered internal rotations this structural feature introduces special fine structure into the rotational spectrum. The existence of a barrier restricting free rotation about the single bond in ethane, a refinement upon the classical principle of organic chemistry, was demonstrated some twenty years ago. Since that time barriers to internal rotation have been detected with fair certainty but measured mostly rather coarsely in a substantial number of molecules. A summary of the currently available data was published during the year by Luft (3). Recent developments signify that the analysis of pure rotation spectra in the microwave region may yield an accumulation of highly refined measures for barriers in the near future.

It has been apparent for some time that the abundant fine structure of transitions connecting a pair of states for external rotation includes components corresponding to molecules in different states of internal rotation. These components can be identified by the variations produced in their relative intensities when the temperature is changed, corresponding to movement of the population distribution through the states for internal rotation. This circumstance has been employed in a number of instances during recent years to evaluate barriers in an obvious way but the results, while a distinct improvement over ones given by former methods, are still rather coarse owing to the errors affecting measurements of relative intensities.

It is an obvious inference from the observation of different transition energies between the same states of external rotation for molecules in different states of internal rotation that there must be an interaction between internal and external rotations. This interaction perturbs slightly the states for external rotation by amounts that are characteristic of the states for internal rotation. A breakthrough in the study of internal rotation has come about through the detailed analysis of this interaction. Although the perturbation

produces only a tiny increment of energy the superlative accuracy attainable in the measurement of frequency in microwave spectroscopy permits the detection of the increment with precision.

The analysis of observations is unavoidably intricate since the positions of the unperturbed levels for external rotation and even to some extent their perturbations by internal rotation depend upon a molecular architecture that must be discovered from the same data. Observations with isotopic species appear to be essential. Moreover, the perturbations caused by internal rotation are not the only ones affecting the states for external rotation. These complications notwithstanding, promising results have been achieved.

Kivelson, in sequels to earlier work, published recently a development of of the Hamiltonian operator for the nonrigid internal rotor (4) and a discussion of nonrigid asymmetric rotors (5), both in connection with the theory of internal over-all rotational interactions. Wilson, Lin & Lide (6) described the calculation of energy levels for internal torsion and over-all rotation in one special class of molecules, those of type CH_3BF_2. Theirs appears to be just the first in a series of related contributions.

We surmise from the following reports concerning other, less symmetrical molecules that the theory has already advanced beyond the stage indicated by published accounts. Kilb (7) in a brief communication states that he has deduced from the data of Solimene & Dailey (8) for methyl mercaptan a barrier of 705 ± 45 cal./mole. This measure of precision is almost three-fold better than the one obtained in the original investigation from the analysis of intensity variations. Swalen (9) in another brief communication reports that the data of Venkateswarlu, Edwards & Gordy (10, 11) for methanol when analyzed in the new way yield a barrier equal to 1110 ± 60 cal./mole. The result for methanol agrees well with the ones given by both Burkhard & Dennison (12) and Ivash & Dennison (13) whose methods are also precise but less generally applicable than the new one. The significance of these measures of precision is not clear to us. Among six separate values for the barrier listed by Swalen the range from greatest to least is only 90 while four of these six values fall within a total spread of only 15 cal./mole. which includes the average for all. The precision measure is reported, nevertheless, as the one we have given above.

In another theoretical investigation along a separate but ultimately related line Burkhard & Irvin (14) have attacked meanwhile the wave equation for internal rotation of two completely asymmetric molecules.

Before closing this report upon the topic of intramolecularly hindered internal rotation we should mention for its novelty that Wagner & Dailey (15) have furnished a proof of the staggered configuration for ethyl chloride. The observed variations of the moments of inertia for its isotopic species require this configuration.

Turning now to another topic in microwave spectroscopy, studies conducted with molecules possessing permanent magnetic moments may hold special interest for physical chemists. Such molecules although familiar are not highly numerous as gases. Sensitive microwave techniques developed

for studies of magnetic hyperfine structure and knowledge gained therefrom concerning simple magnetic molecules may ultimately find application in the investigation of free radical intermediates in reacting systems. Elaborate investigations of the O_2 molecule were reported during the year by Tinkham & Strandberg (16, 17) who find among other things an equilibrium internuclear distance equal to 1.20741 ± 0.00002 A. Studies with NO were described by Dousmanis (18) and also by Mizushima, Cox & Gordy (19). Dousmanis concludes that the unpaired electron is essentially in a $\pi(2p)$ orbital but with a small amount of s-character and with about 35 per cent of its density associated with the oxygen atom. Townes *et al.* (20) discussed the interpretation of hyperfine structure for both of these molecules and also for the OH radical.

Molecular architecture is studied programmatically also through observations upon infrared spectra of gases conducted with instruments having high resolving power. The fund of molecules whose pure rotation spectra might be accessible with this technique is small and has been exhausted so that for the most part today the effort deals with combined rotation-vibration transitions. Nevertheless, except for certain characteristic differences of detail, analysis of the rotational transitions in terms of molecular architecture proceeds in much the same way as for microwave or pure rotation spectra. Moments of inertia are evaluated and again their variations with isotopic substitutions furnish the route to molecular architecture. This pattern of investigations supplements microwave spectroscopy, can compete perhaps in accuracy (see section on techniques), and is applicable to substances that will have no microwave spectrum. It is perhaps less versatile in regard to varieties of conceptual information but it is an important source of information concerning interactions between rotation and vibration. A well known book by Herzberg (21) furnishes an excellent introduction to this topic and also to our next one.

Intramolecular potential energy, more precisely its variation with configuration, is another topic for programmatic investigations. Infrared absorption spectra, obtained usually with instruments of low to moderate resolving power, and Raman spectra are (or should be) observed in parallel. Modal frequencies are tabulated and assigned to excitations of molecular vibrations, either singly or in combinations, taking account of selection rules derived in a formal way from symmetry considerations whenever these are applicable. Correctly identified fundamental frequencies can be used to calculate thermodynamic properties in a familiar way and to evaluate constants in a harmonic representation of the intramolecular potential energy (a general quadratic function of the atomic displacements of small amplitude, consisting of the leading terms in a power series expansion, that occur as the configuration of the molecule vibrates about the equilibrium one). It is possible in principle to construct a detailed picture of the patterns and amplitudes for the atomic displacements corresponding to each mode of molecular vibration from knowledge of all of the constants contained in the harmonic representation for the potential function. These constants are of

interest too as measures for the rigidity of the molecular configuration and for the information they furnish concerning its dynamical articulation. This area of investigation is thoroughly covered in two books: one by Herzberg (21) and another highly welcome, recent one by Wilson, Decius & Cross (22).

The transformation of observed vibration frequencies into a harmonic expression for intramolecular potential energy involves an awkward difficulty. The number of constants in the most general expression for one molecule exceeds the number of its modes of vibration. In smaller molecules this difficulty can be met by turning to isotopic species, whose vibrations are governed presumably by the same potential energy. In larger molecules the procedure as a general practice is impractical; there is no choice but to ignore terms somewhat arbitrarily on grounds of physical and chemical intuition or to replace them by corresponding ones "transferred" from smaller molecules. Some recent contributions may have bearing upon both of these devices for making the problem tractable.

Slowinski (23) proposes the use of a valence force field expanded about a hypothetical "strain-free" configuration rather than the customary equilibrium one. He reports some promising preliminary results with small molecules and it would seem offhand that this notion might well lead to an improved transferability of force constants from one molecule to the next. Coulson & Senent (24) describe an approximate potential function for the "out-of-plane" vibrations for π-electron systems that gives good results when tested on ethylene, benzene and naphthalene although it contains in each case but two force constants.

An important development in the representation of intramolecular potential energy, transcending the harmonic approximation, was described during the year under review by Lippincott & Schroeder (25). They tested a new mathematical formulation for the potential energy of a diatomic molecule as a function of its internuclear separation. With it they achieved a correlation of pertinent data (ones relating to dissociation energy, vibrational frequency, anharmonicity parameter, etc.) for a large number of cases which is markedly superior to that afforded by the familiar and popular Morse function. The new function is simpler in mathematical form and convenient for purposes of computation. It can be adjusted to become infinite at the origin while it approaches a van der Waals' interaction for large separations. The parameters that govern these limiting behaviors obey certain general rules. Lippincott (26) has indicated briefly the possibility of a general quantum mechanical origin for this new and superior empirical function. Its further application to the construction of a successful model for the hydrogen bond will be mentioned later in this article.

The current literature continues to record new and more refined correlations of the empirical kind between vibration frequencies and molecular structure. The status of this programmatic endeavor has been well summarized recently by Bellamy (27) and we shall leave it for the advanced practitioner of the art to find for himself the recent refinements.

Absolute intensities of vibrational transitions are being investigated systematically in a number of laboratories. Reports of new results appear regularly and with increasing frequency. These investigations commence ordinarily with a series of observations, using low to moderate resolving power, upon the infrared absorption by a gas confined under variable, rather high pressures, often produced by addition of a foreign gas. The apparent intensity of absorption is then integrated in a certain way separately under the envelope of each vibration-rotation band. The resulting magnitudes change for each band with the partial pressure of the absorbing gas and also with the total pressure owing to a mixture of both instrumental and intermolecular complications. These complications supposedly can be eliminated without being analyzed when a series of properly conducted observations is extraplated to an appropriate limit. The limiting magnitude is the desired absolute intensity. An alternative experimental approach to the measurement of absolute intensities has been discussed recently by Penner & Aroeste (28).

Magnitudes for absolute intensities, along with an accurately determined harmonic potential function (see an earlier paragraph) and an appropriate analysis, can be manipulated in principle to arrive at conclusions concerning the variations of electric charge distribution that occur within a molecule as it vibrates and even perhaps to achieve some kind of conventional mapping for the time-average distribution of electric charges. This potentiality is inviting but the road in actuality is strewn with difficulties. We venture to suggest that current efforts along these lines should be greeted charitably but with reservations.

The measurement of absolute intensities is a programmatic endeavor, but the interpretation of these quantities conveys to us still the aroma of an exploration. Molecules that have been examined with varying degrees of success during the year under review include:

H_2CO	by	Hisatsune & Eggers (29),
C_2H_4	by	Eggers (30),
BrCl & ICl	by	Brooks & Crawford (31),
C_2F_6	by	Williams, Person & Crawford (32),
C_2H_2 & C_2D_2	by	Wingfield & Straley (33),
CH_2Cl_2	by	Straley (34),
$H_3C—C\equiv C—CH_3$	by	Mills & Thompson (35).

We invite our readers to peruse these contributions and form their own opinions. Some essential background can be found in the book by Wilson, Decius & Cross (22).

An influence of the interaction between rotation and vibration upon the line intensities in vibration-rotation bands of diatomic molecules has been studied theoretically by Herman & Wallis (36) who warn that it may have an important bearing upon spectroscopic measurements of temperature in flames.

Bernstein & Allen (37) propose a standard intensity scale for Raman bands in liquids. General adoption of their carefully defined standard scale would

expedite the accumulation of comparable measures in an important area of observation where they are notably lacking.

Measurements of intensities, mostly for vibrational transitions excited by infrared absorption, are being reported for liquids by investigators whose objectives are in the realm of intramolecular information. Some aim at absolute intensities to be interpreted as outlined for gases above, others at frankly empirical correlations between intensities and molecular structure. We suggest that all such undertakings must be regarded at the present time with suspicion; notable past successes with measurements, interpretations, and correlations of vibration frequencies for molecules observed indiscriminately as solids, liquids, or gases notwithstanding.

Frequencies of vibration mostly are peculiarly insensitive to molecular interactions.

Such is not the case with intensities of absorption. To embark upon measurements of intensities is to enter an intermolecular arena. How deeply we do not yet know.

The Intermolecular Arena

Intermolecular considerations intrude even upon the interpretation of spectra observed with dilute gases. Line shapes in microwave spectra, provided that they are not governed instrumentally by the power levels employed for observation, and in well resolved optical spectra may be governed by the nature and frequency of molecular collisions. Marked sharpening of lines can be observed with molecular beams under transverse observation whereby Doppler and other broadening is effectively reduced or virtually eliminated. Collisions among molecules can be the determinants of lifetimes for rotational states and, through the uncertainty principle, thus also of line widths. The effective collision diameters in such circumstances are dependent upon the natures of molecular interactions.

Adequate interpretations for line shapes involve highly detailed considerations of molecular collisions. During the year under review Smith, Lackner & Volkov (38) developed further for the special case of some linear molecules Anderson's (39) general theory of pressure broadening in the microwave region and concluded after analyzing experimental data for OCS and BrCN that "pressure broadening can serve as a very useful tool in the investigation of intermolecular forces."

Any microscopic theory of pressure broadening must merge ultimately with the macroscopic theory of dielectric relaxation. An interesting experimental and phenomenological exploration of the region intermediate between the two extremes was reported by Phillips (40) who investigated several gases over a wide range of pressures encompassing examples of condensation.

Absorption intensities as well as line shapes are significantly altered in gases confined under high pressures and in liquids or solids. An induced absorption, resulting from molecular interactions, becomes superimposed upon the intrinsic one of intramolecular origin that is observable in the dilute

gas. The induced absorption is immediately obvious when the intrinsic one cannot occur because of selection rules.

The pure rotational spectrum of hydrogen gas, both self-induced and foreign-induced by either carbon dioxide or nitrogen, has been observed with pressures ranging from about 30 to about 100 atm. by Ketelaar, Colpa & Hooge (41). In pure H_2 the intensity of the self-induced absorption varies approximately with the square of the pressure. Under equivalent conditions the absorption induced by N_2 exceeds the self-induced while that induced by CO_2 is still more intense.

A general theory of pressure broadening and self- or foreign-induced absorption was developed from first principles several years ago by van Kranendonk (42). In our opinion it is destined to command increasing attention. Van Kranendonk verified his theory in part by computing, again from first principles, the intensity of a vibrational transition for H_2, both self- and foreign-induced by He, in quite satisfactory agreement with observations by Crawford *et al.* (43).

Self-induced vibration-rotation absorption by H_2 in the gaseous, liquid, and solid states was observed further by Allin, Hare & MacDonald (44) and by Hare, Allin & Welsh (45). The separate transition probabilities for the rotational transitions peculiar to ortho- and para-species were found to be independent of the ortho-para ratio in one set but not so in another.

Simultaneous transitions, ones involving the simultaneous excitations of vibrations in two dissimilar molecules, also are induced by molecular interactions. They have been observed in both gases and liquids.

Absorption was observed with a modal frequency near 7050 cm^{-1} by Coulon, Robin & Vodar (46) in mixtures of HCl and H_2, confined under pressures in the range of hundreds of atmospheres. This is almost exactly the sum (7048) of the fundamental vibration frequencies for H_2 (4162) and HCl (2886). Assignment to a simultaneous transition is supported by observations with N_2 substituted for H_2. Galatry & Vodar (47) have offered a theoretical treatment, but we suspect on general grounds that they overemphasize the importance of polarity in one of the interacting molecules.

Simultaneous transitions were observed in liquids by Ketelaar & Hooge (48) as a sequel to earlier observations of such transitions in gas mixtures, e.g. CO_2+N_2, CO_2+O_2, and CO_2+H_2, by Fahrenfort & Ketelaar (49). Solutions of Br_2 in CS_2 show well defined absorption bands displaced by about 306 cm^{-1} on either side of the strong CS_2 band at 1510; when Br_2 is replaced by I_2 the corresponding satellites appear with displacements of about 203 cm^{-1}. These bands are absent in pure CS_2 while the fundamentals for Br_2 and I_2 in the liquid state are 306 and 203, respectively. The sum and difference transitions have in each case intensity ratios corresponding quite well with the computed population ratios for the originating states. Ketelaar & Hooge (50) reported detection of simultaneous transitions also with liquid solutions of CS_2 in each of S_2Cl_2, PCl_3, PBr_3, $SOCl_2$, $PSCl_3$ and CCl_3SCl. All of these latter substances possess low vibration frequencies, observable in their Raman spectra, whose sums with 1510 cm^{-1} in CS_2 fall in a region that

is otherwise transparent and thus favorable for the observation of simultaneous transitions.

Simultaneous transitions have become within the year a convincingly demonstrated consequence of molecular interactions. They must be recognized henceforth as potentially significant sources of induced absorption by combinations and overtones in spectra for pure substances in condensed phases.

The intensities for infrared absorption bands in liquids diminish with increasing temperature, owing to the effect of expansion upon induced absorption. Slowinski & Claver (51) report briefly upon this phenomenon stating that the effect is often, but not always, quite large, with bands observed at 100°C. having in some cases an optical density about seventy per cent that at 25°C. Unpublished work by Greenwald (52) from our own laboratory indicates that the purely induced absorptions in liquid benzene are affected by temperature in a common way; the integrated induced absorption varies approximately with the square of the liquid density. Generalizing from this result one might expect the intensity of a purely induced absorption to diminish to some seventy or eighty per cent when a typical liquid is brought from room temperature to 100°C and otherwise to be less affected in proportion to any intrinsic absorption upon which the induced one is superimposed.

Induced absorption, including simultaneous transitions, has been demonstrated in non-polar liquids or gases and in solutions formed from them. It occurs in solids, too. Purely induced absorption in liquids or solids often appears with medium or even greater intensity on the qualitative scale. Polarity is not a dominant requirement in order that molecular interactions induce or modify the probabilities of spectroscopic transitions and polar substances do not seem especially to exalt the intensities of induced absorptions. This accords with much other experience with molecular interactions, for example in the theory of cohesive energy and its extension to regular solutions.

One consequence of molecular interactions has been envisaged macroscopically as an effect by a surrounding dielectric upon the transitory dipole moment of intramolecular origin that governs the intensity of an intrinsic absorption. This multiplicative effect upon intrinsic absorption could occur quite apart from the additive one from induced absorption. Polo & Wilson (53) have clarified a discrepancy between previous theories of this effect, and they conclude that an intensification by some thirty per cent should be expected to accompany liquefaction in a typical substance (refractive index about 1.4–1.5). They indicate, however, that the experimental evidence is not conclusive and stress the need for more experimental work.

Molecular interactions are strongly involved in the Fermi resonance for two, neighboring excited vibrational states in CCl_4. Tuomikoski (54) observed that both relative intensities and frequency displacements change as CCl_4 is liquefied and change again when it is dissolved in various organic liquids. Liquid benzene exhibits (52) an example of Fermi resonance that is

markedly affected by changing temperature, presumably on account of the parallel change of molecular interactions.

Brandmüller (55) reports that a line breadth in the Raman effect, associated in gases with contributions from rotational transitions, is some four- to five-fold smaller in liquids than in gases. He attributes the discrepancy to molecular interactions and the structure of the liquid state. The sharpening indicates definitely in our experience the onset in the liquid of some kind of correlation among the rotational degrees of freedom for individual molecules.

Infrared absorption bands, especially ones for purely induced transitions, often are spectacularly sharp in molecular crystals. Molecular interactions in a liquid erase the characteristic PQR branch structure of vibration-rotation bands observed in gases but do not alter greatly the band width; in molecular crystals they can reduce the bands to mere lines. Indeed, we have seen many absorption envelopes observed with crystals that are best interpreted as the contours of the radiation samples furnished by the monochromator. This sharpening is connected theoretically with a correlation of similar motions executed by different molecules in a crystal, theoretically a dynamical consequence of its periodic structure.

Purely induced absorption may either persist, then usually intensified, or vanish again when a liquid is crystallized. The mechanism of induced absorption depends upon the arrangement of molecules, in addition to their distances of separation, in a condensed state. It is now well known that selection rules can be formulated for vibration spectra of crystals in terms of the symmetries of their arrangements.

Vibration spectra of molecular crystals will contain, according to these selection rules, fine structure caused by molecular interactions. The pattern of fine structure is governed qualitatively in an ideal crystal by the symmetry of the crystallographic arrangment in relation to any intramolecular symmetry; it is governed quantitatively by the intensities of molecular interactions. In strongly interacting arrays the spacings are measureable but small, in weakly interacting ones they usually are not resolved. In biaxial crystals the absorption by each fine structure component is polarized along a characteristic direction, in the orthorhombic system always a crystallographic axis. Fine structure components sometimes can be studied individually, also in uniaxial crystals, even when they are not resolvable directly, by suitably conducted observations with single crystals in polarized radiation. When the intramolecular oscillations of constituent molecules are adequately understood the multiplicities and polarizations of the fine structure components for each may be predicted, but not the small separations; relative intensities of fine structure components may be predicted for the intrinsic contribution to absorption but not for the induced part.

Observations upon fine structure in crystal spectra are undertaken to study molecular interactions in well chosen systems, to fill gaps in our knowledge of crystallographic arrangements or of molecular structures and vibrations, or for some combination of these reasons.

For example, Hornig & Osberg (56) employed this approach recently to

investigate the arrangement of H atoms in crystals of hydrogen halides and obtained measures of the molecular interactions. Busing (57) studied the arrangement of H atoms in NaOH and found, incidentally, an interesting dissimilarity between it and NaOD. Pimentel *et al.* (58–60) examined naphthalene, whose molecular structure and crystallographic arrangement are known beyond dispute, in an effort to identify the intramolecular symmetry species for each of the highly numerous frequencies appearing in its spectrum. $B(OH)_3$ was studied by Bethell & Sheppard (61) and the ion OH_3^+ by Ferriso & Hornig (62).

Insofar as such investigations employ only selection rules and observations of multiplicities their conclusions are potentially exact. When relative intensities of fine structure components are invoked, however, without correcting for the momentarily unpredictable contributions from induced absorption, the conclusions become debatable and even unreliable. Having ourselves conducted such endeavors in the past, we offer our criticism charitably. Caution is necessary. Among other things, the quantitative comparison of apparent intensities observed for lines having unknown and probably different natural widths, comparable with and perhaps narrower than the spectral slit, is not likely to be meaningful. Also, the apparent anisotropies of induced absorptions, in certain cases where we have knowledge, do not resemble those for intrinsic ones.

In naphthalene, for example, where induced and intrinsic absorption occur superimposed throughout most of the spectrum, carefully refined measurements of absorption anisotropies by Ichishima & Blanc (63) show easily detected, large, and variable discrepancies from what would be expected for intrinsic absorption alone. Indeed, the variability is so great that we would be unable to identify with assurance in any case the intramolecular symmetry species of the intrinsic absorption.

Observations of the anisotropies for five examples of purely induced absorptions in a single crystal of benzene were reported recently by Zwerdling & Halford (64). For these examples of purely induced absorptions the anisotropies are all highly similar, perhaps even identical, although quite different sorts of intramolecular motions are being perturbed.

Purely induced absorption occurs again quite frequently in the infrared spectrum for a single crystal of cyclopropane, grown and observed recently in our laboratory by Krikorian, Brecher & Blanc (65). Once more, the patterns of anisotropies for purely induced absorptions are markedly different from ones for the intrinsic variety. Broad bands, resulting from concomitant transitions among lattice vibrations, occur throughout the vibrational spectrum observed by Krikorian (66) with a single crystal of acetylene. Both parallel and perpendicular type bands are polarized similarly, a circumstance that would seem inexplicable in terms of intrinsic absorption alone.

Consequences of molecular interactions, such as we have just been describing, are detected easily as aberrations in the relative intensities of components of absorption although in all of these cases the interactions are too weak to cause significant spacings within the fine structure. Where interac-

tions are strong enough to cause resolvable fine structure it seems likely that aberrations of intensities associated with contributions from induced absorption will become even more important.

Fine structure in crystal spectra arises from the coupling of similar motions executed by different molecules in the lattice (also, but trivially for our present purposes, from removal of intramolecular degeneracy of vibrations). Decius (67), utilizing dilution of a lattice with isotopic species to modify coupling, demonstrated recently in an admirably simple way, both experimentally and theoretically, the marked sensitivity of intensities and the comparative insensitivity of frequencies to the details of this coupling.

Lattice defects in general, any aspects of disorder, modify fine structure, its anisotropy, band contours and finally even selection rules. Real crystals always differ, whether in greater or lesser ways, from the ideals employed as models for the construction of the spectroscopic theory that we now possess. As time passes we must expect to see an increasing fund of "exceptional" observations, leading ultimately to improved theories that will embrace them. Indeed, a number of examples of exceptional spectra for strongly interacting constituents exist today although we are not aware of any in the category of molecular crystals. Lax & Burstein (68) have attempted recently to deal with some of the known exceptions while Rosenstock (69) has attempted to assess the natures and likelihoods of observable consequences from presently faulty idealizations of crystal boundaries. Long range prospects for spectroscopic investigations of lattice defects appear to us to be very bright, but there is much to be done still in the elucidation of "first-order" phenomena before we can safely concentrate attention upon the manifestations of defects.

Polymers can be idealized as one dimensional crystals with strong interactions between the monomeric constituents, copolymers as such with lattice defects. Theory developed and tested successfully with crystals can be specialized to one dimensional cases and applied to polymer spectra. Tobin (70) has done this recently to produce a systematic theory of selection rules and multiplicities for chain molecules. Conversely, simplicities inherent in the one-dimensional case invite the construction of quantitative theories concerning intensities, frequency displacements caused by coupling, and the like, that may serve as useful prototypes for generalization to the three-dimensional case, to be tested with polymers in a unique way by systematically varying the length of chain. Notable developments along these lines by Brown, Sheppard & Simpson (71) and by Primas & Günthard (72) were covered in the previous review of this series. The systematics of intensities were attacked during the current year by Primas & Günthard (73). A number of recent articles bear upon the magnitudes of the frequency displacements caused by coupling: Bratož (74); Stein (75); Higgs (76); Nakagawa (77).

Molecular interactions restrict rotations of molecules to librations in crystals. When moments of inertia are small and interactions strong the frequencies of libration become large enough to be easily detected and meas-

ured via librational transitions concomitant with vibrational ones. Plumb & Hornig (78) have completed a series of comparative observations and interpretations of the librations by NH_4^+ in ammonium halides with a report upon NH_4F. Librational transitions were observed directly in crystalline HCl and HBr by Osberg & Hornig (56).

Internal rotation is modified by molecular interactions, profoundly so in the solid state. Rotational isomers exist from the spectroscopic viewpoint whenever restriction of internal rotation results in librations about first one, then another of distinguishable configurations differing by an increment of internal rotation. "Well-defined" states and corresponding frequencies for the molecular vibrations will differ somewhat according to which configuration is being stabilized momentarily by the potential energy restricting internal rotation. The observed vibration spectrum will consist of a superposition of ones corresponding to the different rotational isomers in proportions determined by their statistical abundances. The situation is recognized in practice when modal frequencies are found to be unusually numerous for a molecule of the general class while sets of these frequencies are observed to become uniformly more and less intense when spectra are compared at different temperatures or for different physical states. All but one of these sets is completely erased ordinarily in the spectrum for the solid state; only a single isomer is present usually in the solid state.

Molecular interactions in the solid state apparently superimpose upon the potential energy restricting internal rotation intramolecularly a substantial, indeed a predominant intermolecular contribution. It is worthy of notice too that very often the isomer stabilized by the crystal is a non-polar, rather than a polar one.

Rotational isomerism in symmetrically substituted ethanes has been under programmatic investigation now for a number of years, especially by Mizushima (79) and his numerous collaborators. The trans-isomer is often the exclusive constituent in crystals of these substances where it can be identified by selection rules that govern the observed spectra for the solid. The trans-isomer is often also the slightly stabler one in the liquid and vapor, both of which contain the gauche-isomer in similar but not identical proportions, but in these phases the distinction is not great and either isomer may predominate. Compared with the solid, molecular interactions in the liquid state have only a small influence upon the proportions of isomers that coexist in the vapor state.

Some interesting contrasts of behaviors were reported during the year. Kagarise (80) found that the trans-isomer of 1,1,2,2, tetrabromoethane has the higher energy in the liquid although it still is the only isomer present in the crystal. In the corresponding tetrachloroethane the trans-isomer has again the higher energy in the liquid, but now it is the gauche-isomer that occurs exclusively in the crystal [Naito *et al.* (81)].

Kagarise & Daasch (82, 83) reported that the trans-isomer of 1,2 dibromo-1,1,2,2 tetrafluoroethane has the lower energy in both liquid and

vapor and imply that it is present exclusively in the solid but for 1,2 difluoro-1,1,2,2, tetrachloroethane they reported that there is no detectable change of relative intensities within its spectra accompanying either change of temperature or solidification although the modal frequencies seem much too numerous for a single isomer. We share their perplexity.

Two brief communications allege the coexistence of isomers in a solid phase. Janz & Fitzgerald (84) observed an abrupt, isothermal change in the infrared absorption spectrum for crystalline succinonitrile but no significant change at the melting point. They interpret their observations to mean that there is only a single isomer in the solid phase below −44°C. but that two coexist in the solid and also the liquid at higher temperatures. We find the interpretation unconvincing; without any greater amount of information it seems more plausible to suppose merely an abrupt crystal structure transition accompanied by a change of selection rules. We would not exclude the possibility that a change of molecular configuration accompanies the change of crystal structure but we see no compelling evidence for coexisting isomers. Yoshino (85) states that spectra for solutions of 1,4 dichlorocyclohexane contain bands whose relative intensities change with solvent and that these same bands persist in the pure solid but with relative intensities that change markedly and continuously with its temperature. He interprets the observations as evidence for isomers coexisting in a solid phase. Yoshino reports no data, and we refrain from further comment.

Molecular interactions in a homologous series of polymethylene halides studied by Brown & Sheppard (86) stabilize in the solid isomers with non-planar skeletal configurations when the chains are short. Longer chains appear to be stabilized in crystals with fully extended skeletons. Trimethylene iodide was obtained and observed in two crystalline forms, a metastable one containing the isomer with planar skeleton and a stable one containing a non-planar isomer.

Molecular interactions involved in the mechanism of adsorption can be studied spectroscopically now as a result of recent advances in techniques. For example, Yates, Sheppard & Angell (87) reported evidence for unusually strong hydrogen bonding when ammonia is adsorbed by silica glass. Yoshino (88) states that the abundance ratio for the rotational isomers of 1,2 dichloroethane is affected slightly, in the direction caused by dissolving the substance in a polar liquid, while the ratio of keto- and enolisomers, along with the spectrum for the enol-form, is affected grossly by adsorption of acetyl acetone on silica gel. Strong hydrogen bonding is indicated in the latter instance again. Pliskin & Eischens (89) have pointed out some possible pitfalls for the unwary.

Hydrogen bonding, uniquely among molecular interactions, causes a gross displacement downward in the magnitude of the hydrogen "stretching" frequency. The amount of this displacement can be literally spectacular: in extreme examples the OH frequency expected normally near 3700 falls below 2000 cm^{-1}. Hydrogen bonding causes also a marked broadening (300–400

cm.$^{-1}$) of the absorption band, a broadening that is not sensitively related to the amount of the frequency displacement. These phenomena are quite extraordinary within the findings of empirical spectroscopy.

Rundle & Parasol (90), likewise Lord & Merrifield (91), discovered independently several years ago that the magnitude of the frequency shift was connected systematically in crystals with the distance separating the two heavy atoms joined by the hydrogen bond.

Lippincott & Schroeder (92), using the new internuclear potential function that we remarked upon earlier (25), have now constructed a one-dimensional dynamical model for the hydrogen bond in crystals that explains well its unique spectroscopic properties. With resort to only one spectroscopic observation upon hydrogen bonds they predict in excellent agreement with available observations how both the OH distance and its stretching frequency depend upon the O—O separation. With aid from a second observation upon energies they successfully predict further how such energies vary with the O—O separation and also the vibration frequency for the heavy atom pair. The utility of the model is impressively demonstrated.

Vibration spectra afford now as a result of these developments a speedier and yet more precise means for measuring OH as well as O—O separations along with hydrogen bond energies. Frequency displacement occurs at the rate of about 500 cm.$^{-1}$ for each 0.1 A of change in the distance separating the ligands or for each kcal. of bond energy!

The broadening of the absorption that accompanies hydrogen bonding seems to be connected in a general way with the sensitivity of the frequency to the O—O separation along with a slowly changing potential energy governing the movements of this pair. The lattice will be prone to defects for this reason and also because of the multiplicity of positions for the H atoms as well.

The valence angle in hydrogen bonding continues to invite speculations [Krimm (93); Rundle, Nakamoto & Richardson (94)].

The intermolecular arena of vibration-rotation spectroscopy is already a large and important one. It is developing rapidly.

Techniques

A standard notation for the spectra of polyatomic molecules has been under consideration by an international committee now for some time. The committee recently published a report (95) bearing upon notation in all areas of spectroscopy.

New techniques for ultra-high resolution microwave spectroscopy were reported during the year. These techniques achieve improved resolution by conducting observations under specially arranged conditions where the natural widths of lines are made unusually small. Dicke & Romer (96, 97) observe emission during the spontaneous, radiative decay of a photostationary state created by a prior pulse of power. The observed line is narrower in the absence of power and also in their experiments because a special design of cavity reduces Doppler broadening by selective removal of

faster moving molecules. Dicke & Romer achieve lines having about one-fourth of the usual Doppler width.

Gordon, Zeiger & Townes (98) reported further upon the "maser" (microwave amplification by stimulated emission of radiation), and upon its extraordinary resolution. This device observes the emission of radiation accompanying the attainment of thermal equilibrium among states whose relative populations were modified by selection with an inhomogeneous electric field which preferentially deflects one of these states out of a directed molecular beam. The beam virtually eliminates Doppler broadening while the weak stimulation of emission produces otherwise an extremely narrow line. The maser is a versatile device, serving at will as amplifier, spectrometer or oscillator. As an oscillator it exhibits frequency stability of the order of 4 parts in 10^{12} during one second intervals and 1 part in 10^{10} over an hour. As a spectrometer, Gordon (99) has achieved with the maser the resolution in the inversion spectrum of NH_3 of magnetic hyperfine structure caused by reorientations of the proton spins.

In the near infrared region the Fabry-Perot interferometer has been adapted ingeneously for spectroscopy by Jaffe, Rank & Wiggins (100, 101) who report that a region many times the spectral range of the interferometer can be displayed directly and unambiguously without overlapping orders. They report an achieved, full resolution of 0.043 $cm.^{-1}$ in the vicinity of 6700 $cm.^{-1}$, a separation less than three times the Doppler widths of the resolved lines. The achievement represents a six-fold improvement over the grating alone and compares well with Greenler's (102) prediction for a theoretical advantage of about five. Greenler suggests also that multilayer films of Te and KBr, having high reflection combined with low absorption, appear to be well suited for extending the practice of infrared interferometry.

The interferometer has been examined also from the standpoint of Raman spectroscopy by Dupeyrat (103).

Instrumentation and techniques generally appropriate to spectroscopy in the near infrared were reviewed by Kaye (104) whose summaries of technical information will be of interest to investigators seeking to improve observations at longer wave lengths.

Blout & Abbate (105) report that a double-beam infrared microspectrometer can be achieved quickly and easily with a suitable attachment to a conventional double-beam instrument and affords a five-fold saving of time.

A fast Raman spectrometer was described by White, Alpert & DeBell (106) who designed it for small liquid and gas samples. Observations of the Raman effect in gases at low pressures should be greatly expedited by a new cell, incorporating multiple reflections, and other techniques described by Welsh *et al.* (107).

An outstanding development is the growing availability of excellent, small gratings designed to be substituted for the Littrow mirror in the popular, commercial infrared spectrometers that abound today in all chemical laboratories. These gratings promise both greatly to extend the range and to improve the resolution afforded by these ubiquitous instruments.

Suitable gratings can be purchased today for some spectral regions and are in immediate prospect for all, priced well below the cheapest of the prisms they replace. Lord & McCubbin (108), with the aid of a photoconductive detector, achieved resolution of 0.3 $cm.^{-1}$ or less in the region 2000–3000 $cm.^{-1}$. Plyler & Acquista (109), using the conventional globar source and unmodified amplifier with thermocouple detection, apparently achieved with coarse gratings (fewer than 10 lines/mm) the resolution of 1 $cm.^{-1}$ both at 100–200 and at 300–400 $cm.^{-1}$. Rumors are rife of quantum process detectors that function and improve sensitivity also at the longer wave lengths. Overlapping of orders is still a problem but we think not an insuperable one now that such strong incentive exists to promote the search for filters. Another revolution seems to be in prospect in this area of techniques and observations. Higher resolution spectroscopy will become commonplace.

Our weapons improve steadily in speed, power and sharpness.

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EXPERIMENTAL MOLECULAR STRUCTURE[1]

By San-ichiro Mizushima and Takehiko Shimanouchi

Chemical Laboratory, Faculty of Science, Tokyo University, Tokyo, Japan

Bond lengths, bond angles, and internal rotation angles are the three important factors determining the geometrical structure of a molecule. This review is concerned with recent investigations which have led to the experimental values of these molecular constants, and their transferability. From this point of view there are several other molecular constants which have aroused a great deal of interest. Of these we shall discuss to some extent force constants obtainable from spectroscopic data.

Limitations of space render it impossible to make reference to all the interesting work that has appeared in the fields mentioned above. Furthermore, owing to the reviewers' geographical location, it has not been possible to mention some papers that appeared later than November 1955.[1]

Bond Length

The diffraction of radiation with wavelengths comparable to molecular dimensions has been applied widely to the determination of bond lengths in individual molecules and in crystals. In the case of simple molecules spectroscopic methods, particularly the microwave technics and the rotational Raman measurements, provide us with very precise values of bond lengths.

The results published in 1955 are summarized in Table II. The experimental values obtained by different methods agree with one another satisfactorily.

As is well known by the use of rotating sectors the accuracy of the electron diffraction measurement has been considerably improved (101, 102). The data obtained by Karle (1) for the diatomic molecules, O_2, Br_2 and I_2 are in good agreement with those of spectroscopic measurements. For I_2, however, he found an anomalous electron scattering at a certain applied voltage, which should be taken account of in the interpretation of the data obtained (1). For CH_3Cl (17, 103) and CH_3CN (37, 47) the results of the electron diffraction measurements are in good agreement with those of the microwave investigations. The microwave measurement of CF_3Cl was not sufficiently complete for the determination of the molecular structure, but yielded moments of inertia in agreement with the electron diffraction data recently obtained by Bartell & Brockway (17). In this diffraction experiment a refined procedure which compensates for the interference arising from non-nuclear scattering has been used. Furthermore, the effect of the anharmonicity of vibration was taken into account and a method was presented to obtain

[1] The survey of literature pertaining to this review was completed in November, 1955.

from the apparent bond lengths, r_0, the actual equilibrium values, r_e (16). The mean vibrational amplitudes obtained according to this method are in good agreement with those of the approximate calculations by Morino *et al.* (104).

Stoicheff found the C—C bond length of C_6H_6 to be 1.397 Å by the measurement of the rotation Raman band (105). However, a definitely smaller value 1.378 Å was obtained from the preliminary account of the result of the x-ray measurement in the crystalline state by Cox & Smith (106). This discrepancy can be explained, if the anisotropic thermal motion in the crystal, especially the rigid-body oscillation about the hexagonal axis, is taken into account. The value corrected by Cox *et al.* (51) becomes 1.392 Å which is in good agreement with that of the Raman data. [See also Hughes (106a).] In Table II are shown data of molecules containing planar rings, e.g., indanthrone, ferrocene and triazine. For some of them the nature of bonds has been discussed in relation to bond lengths.

From the microwave measurements the moments of inertia of the molecule are obtained. For the simplest molecules the evaluation of the moments of inertia of a single molecular species is sufficient for a complete determination of the structure. However, for the majority of molecules this is not sufficient and we have to employ isotopic species on the assumption that the bond lengths are the same for molecules which differ only in isotopic content. Many of the values of bond lengths and bond angles shown in Table II have been obtained by the use of this isotopic effect.

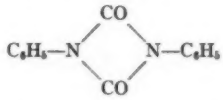
In some of the molecules, the question of the planarity has aroused considerable interest. This can be solved by knowing the values of principal moments of inertia of the molecule obtainable from the microwave measurement. Thus Kurland (50) established the planar structure of the formamide molecule in the gaseous state, although the double bond character of the C—N bond of the gas molecule is less than that of the liquid molecule (107, 108). Fernandez, Myers & Gwinn (32) discussed the out-of-plane contribution to the moments of inertia of trimethylene oxide on the basis of the microwave data.

The planarity of the amide structure has been an interesting subject in relation to the structure of proteins. The planar trans structure of *n*-methylacetamide has been proved by Raman, infrared, ultraviolet, and dipole measurements (109). The same structure of the peptide bond has been shown by x-ray crystallographic studies for glycylglycine, acetylglycine, etc. (110) and also for tetradecane amide (75), diacetylhexamethylene diamine (76) and polycaproamide (79) shown in Table II. Marsh, Corey & Pauling concluded that the structure of silk fibroin (80) and Tussah silk fibroin (81) is described by antiparallel-chain pleated sheets.

The structures of almost all amino acids individually or as part of simple peptides commonly occurring in proteins have been established or are currently being investigated. An exception is arginine, for which no structure determination has been reported. In connection with this the results of struc-

ture determination of creatine monohydrate by Mendel & Hodgkin (111) and Jensen (62), and methylguanidinium nitrate by Curtis & Pasternak (64) are significant. The guanidinium radical in these molecules has been shown to exhibit almost perfect trigonal planar symmetry.

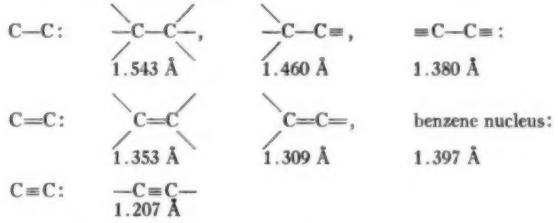
The peptide bond of a ring molecule can not take the *trans* form, so far as the ring is small, e.g. δ-valerolactam and ϵ-caprolactam (124). Brown showed that in the phenyl isocyanate dimer



the peptide structure takes the *cis* form and the C—O and N—C_6H_5 bonds make angles of 87.5° and 79° with the normal to the central four-membered ring, respectively (78).

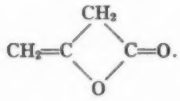
The transferability of bond lengths (and co-valent radii) from one molecule to another with similar structure has been shown by Pauling (112), Schomaker & Stevenson (113), Gordy, Smith & Trambarulo (114), and others. Small systematic deviations have been found by recent measurements of bond lengths. For example, the C—F bond length becomes less with increasing number of F atoms, e.g. $CH_3F \rightarrow CF_4$ (112, 114, 114a). (See also other fluorine compounds, data for which are shown in Table II.) A similar but less pronounced tendency has been found for the C—Cl length. It is interesting that the C—Cl length of CF_3Cl observed by Bartell & Brockway (17) is less than that of CCl_4.

The carbon-carbon bond lengths are affected by the nature of adjacent bonds. Herzberg & Stoicheff summarized the data as follows (41):

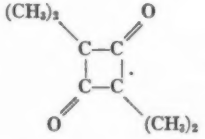


The values of the C—C bond length in three- and four-membered rings have been discussed by Bregman & Bauer (33). Those of spiropentane, cyclopropane, cyclopropene, ethylene oxide and the substances with three membered rings shown in Table II have been found to lie in the range 1.47 to 1.52 Å. The shortening of the bond length from the normal value has been attributed by Coulson & Moffitt (115) to the presence of "bent bonds" in which the line of maximum bonding electron density is outside the direct line joining the nuclei.

In four-membered rings the abnormalities in bond lengths seem uniformly toward longer internuclear distances. This has been attributed to repulsions of the non bonded ring atoms. From an x-ray crystallographic study Lipscomb & Katz (116) showed the ketene dimer to take a lactone configuration



The same conclusion was reached by Bregman & Bauer (33) for this substance in the gaseous state. This is interesting in view of the fact that the dimethylketene dimer was found by these investigators to take symmetrical diketone configuration



The effect of adjacent bonds on the C—H length is less than that on the carbon-carbon length. For the Si—H bond length the same value 1.48 Å has been found for both SiD_3H (82) and SiH_3D (117).

Bond Angle

In methane, the carbon bond angle is 109°28′. The substitution of hydrogen atoms does not much affect this value. The data listed in Table II show that almost all the bond angles (of the carbon atom with four single bonds) lie in a narrow range 109°28′ ± 1°. The result obtained for the Si bond angle is similar to this.

However for molecules of the water type or ammonia type, the constancy of bond angles is not so marked. In Table I are shown the results recently obtained, including those listed by Mulliken (118).

TABLE I

Bond Angles in the Molecules of the Water and Ammonia-Type

H_2O	105° 3′	F_2O	101°	Cl_2O	110.8°	CH_3OH	108°		
H_2S	92° 16′			Cl_2S	102°	CH_3SH	100° 20′	$S(CH_2C_6H_5)_2$	109°
H_2Se	91°							$Se(CH_2C_6H_5)_2$	106°
				Br_2Te	98°			$Te(CH_2C_6H_5)_2$	101°
NH_3	106° 46′	NF_3	102° 9′						
PH_3	93° 18′	PF_3	102°	PCl_3	100° 7′	PBr_3	101°	PI_3	100°
AsH_3	91° 50′	AsF_3	102°	$AsCl_3$	98° 25′	$AsBr_3$	101°	AsI_3	100.5°
SbH_3	91° 18′			$SbCl_3$	99.5°	$SbBr_3$	97°	SbI_3	98.5°

Bond angles close to 90° have been found for H_2S, H_2Se, PH_3, AsH_3, SbH_3. This is to be expected from the simple theory of directed valence. On replacement of H by F, Cl, Br, etc. the observed bond angles become greater than 90°. This can be attributed to the repulsive force between these non bonded atoms which is greater than that between hydrogen atoms. The larger values of bond angles are compatible with the values of the force constants calculated from the observed vibrational frequencies of the halogen-substituted molecules (119 to 123). The bond angles observed for CH_3OH, CH_3SH, CH_3NH_2, $S(CH_2C_6H_5)_2$ can be explained similarly.

The repulsive force between the non bonded hydrogen atoms in H_2O or NH_3 would not be large (119 to 123), whereas the bond angles in these molecules are much larger than 90° as shown in Table I. This fact can be understood qualitatively in terms of partial s, p hybridization. However, no adequate explanation seems to have been offered to discriminate between this case and that of H_2S, H_2Se, PH_3 and AsH_3 having angles close to 90°. Mulliken has discussed this problem by using molecular orbital and valence bond theory (118).

Equilibrium Angle of Internal Rotation

For the complete determination of the geometrical structure of molecules, we need information of equilibrium angles of internal rotation in addition to that of bond lengths and bond angles discussed above. The experimental data obtained prior to 1953 have been described in a book by Mizushima (124). Furthermore, in recent volumes of *Annual Reviews* and in *Science Progress* some space has been devoted to a discussion of this problem (125–127).

The so called "principle of free rotation" in organic chemistry was founded upon the nonexistence of isomers whose structures could pass into one another by means of the internal rotation about a single bond: it did not assume that all the positions to which it could lead were equally favorable. Actually considerable evidence based on the spectroscopic, dielectric and thermal measurements has been accumulated to indicate that the rotation is not free and there are in general two or three potential minima in one complete rotation. The rotational isomers corresponding to the minima will rapidly change into one another and any attempt to separate them by the usual chemical methods will not succeed.

In ethane $H_3C \cdot CH_3$, the simplest molecule with an internal rotation axis, the potential minima have been found to correspond to the three equivalent staggered forms. Additional evidence in support of this conclusion has been obtained by the study of rotation-vibration Raman bands by Romanko, Feldman & Welsh (128). However, in substituted ethanes the internal rotation generally produces distinct isomers, e.g. in symmetrically disubstituted ethanes $XH_2C—CH_2X$, there are two forms: One is the *trans* form with the C_{2h} symmetry and the other two are the *gauche* forms which are of lower symmetry (C_2) and are obtained from the *trans* form by internal

TABLE II

BOND LENGTHS AND BOND ANGLES REPORTED IN 1955

Molecule	State	Method	Bond lengths (Å) and angles	References
I_2	gas	ED	r(I—I) = 2.662	(1)
Br_2	gas	ED	r(Br—Br) = 2.290	(1)
O_2	gas	ED	r(O—O) = 1.208	(1)
HBr, HI, DI	gas	FIR	rotational constants	(2)
NO	gas	IR	r_e(NO) = 1.1503	(3)
CO_2	gas	IR	rotational constants	(4)
D_2O	gas	IR	rotational constants	(5)
HDO	gas	MIW	rotational constants	(6)
H_2S	gas	IR	rotational constants	(7)
HDS	gas	IR	rotational constants	(8)
H_2Se	gas	FIR	r(H—Se) = 1.47, ϕ(HSeH) = 91°	(9)
$(CH_3)_2Se$	gas	ED	r(CH)/r(Se—C) = 1.09/1.97 (assumed), r(Se—C) = 1.977, ϕ(C—Se—C) = 98 ± 10°, ϕ(H—C—Se) = 110.5° ± 3.5°	(10)
H_2N—OH	crystal	XD	r(N—O) = 1.47$_6$	(11)
AsH_3, AsD_3	gas	MIW	r(AsH) = 1.5192, ϕ(HAsH) = 91° 50′ (assumed), r(AsD) = 1.5145, ϕ(DAsD) = 91° 30′ (assumed)	(12)
CS	gas	MIW	r(CS) = 1.5349	(13)
SbH_3, SbD_3	gas	MIW	r(Sb—H) = 1.7073, ϕ(HSbH) = 91° 18′, r(Sb—D) = 1.7021, ϕ(DSbD) = 90° 56′	(14)
CD_4	gas	IR	r_e(CD) = 1.095	(15)
CCl_4	gas	ED(S)	r(C—Cl) = 1.769, r_e(C—Cl) = 1.760	(16)
CH_3Cl	gas	ED(S)	r(C—H) = 1.11, r(C—Cl) = 1.783, ϕ(HCH) = 110°	(17)
CF_3Cl	gas	ED(S)	r(C—F) = 1.328, r(C—Cl) = 1.751, ϕ(FCF) = 108.6°	(17)
CH_3OH	gas	MIW	r(OH) = 0.956, r(CO) = 1.427, r(CH) = 1.096, ϕ(HCH) = 109° 2′, ϕ(COH) = 108° 52′, r(O—CH_3 axis) = 0.083	(18, 18a)
CH_3OH	gas	MIW	r(OH) = 0.967, r(CO) = 1.428, r(CH) = 1.098, ϕ(HCH) = 109° 6′, ϕ(COH) = 107° 16′	(19)
CH_3SH	gas	MIW	r(CH) = 1.1039, r(SH) = 1.3291, r(SC) = 1.8177, ϕ(HCH) = 110° 16°, ϕ(CSH) = 100° 16′, ϕ(CS bond-axis of CH_3) = 27.5′	(20)
CH_3SH	gas	MIW	r(CH) = 1.1045, r(SH) = 1.3298, r(CS) = 1.8170, ϕ(HCH) = 110°10′, ϕ(CSH) = 100° 20′	(21)
CH_3NH_2	gas	MIW	r(CH) = 1.093 (assumed), r(NH) = 1.014 (assumed), r(CN) = 1.474, ϕ(HCH) = 109° 30′, ϕ(HNH) = 105° 50′, ϕ(CNH) = 112° 10′, ϕ(CN bond-axis of CH_3) = 3° 30′	(22)
C_2F_6	gas	ED(S)	r(C—F) = 1.32, r(C—C) = 1.56, ϕ(CCF) = 109.5°	(23)

ED = electron diffraction,
ED(S) = electron diffraction measured with rotating sector,
XD = X-ray diffraction,
IR = infrared spectrum,
FIR = far infrared spectrum,
R = Raman spectrum,
MIW = microwave spectrum,
r = bond length
ϕ = bond angle,
r_e = equilibrium bond length

FIR = far infrared spectrum,

r_e = equilibrium bond length

TABLE II (*continued*)

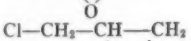
Molecule	State	Method	Bond lengths (Å) and angles	References
$CH_3—CH_2—F$	gas	MIW	The best fit: r(CH) = 1.091, r(CC) = 1.540, r(CF) = 1.375, ϕ(FCC) = ϕ(HCH) = 109° 28′	(24)
$CH_2D—CH_2—Cl$	gas	MIW	rotational constants (staggered configuration)	(25)
$CH_3—CH_2—Br$	gas	MIW	rotational constants	(26)
C_3H_5X, C_4H_9X (X = Cl, Br, I)	gas	ED	bond lengths and angles	(27)
	gas	IR	r(cc) = 1.524	(28)
			r(C—C) = 1.480, r(C—N) = 1.488, r(C—H) = 1.083, ϕ(C$_s$ND) = 112°, ϕ(H$_2$CC) = 159° 25′, ϕ(HCH) = 116° 41′, r(N—D) = 1.000 (assumed)	(29)
	gas	MIW	The best fit: r(C—H) = 1.09, r(C—C) = 1.47, r(C—Cl) = 1.755, ϕ(HCH) = 109°, ϕ(HCCl) = 109°	(30)
	gas	ED	bond lengths and angles	(31)
	gas	ED	bond lengths and angles	(31)
	gas	MIW	rotational constants	(32)
	gas	ED	r(C=O) = 1.19, r(O—CH$_2$) = 1.45, r(O—CO) = 1.45, r(CH$_2$—CO) = 1.53, r(CH$_2$—CH$_2$) = 1.53, ϕ(O—C—C) = 94°, ϕ(C—O—C) = 89°, ϕ(O—CO—C) = 94°, ϕ(C—C—C) = 83°, ϕ(O—C=O) = 123°, ϕ(C—C=O) = 143°	(33)
	gas	MIW	rotational constants	(34)
	gas	ED	bond lengths and angles	(33)
	gas	ED	bond lengths and angles	(33)

TABLE II (*continued*)

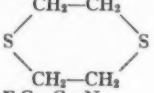
Molecule	State	Method	Bond lengths (Å) and angles	References
Cyclopentanone	gas	MIW	rotational constants	(35)
	crystal	XD	r(S—C) = 1.80, 1.82, r(C—C) = 1.49, ϕ(CCS) = 112.6°, 112.8°, ϕ(CSC) = 99.0° chair configuration	(36)
$F_3C—C\equiv N$	gas	ED	r(C—F) = 1.33, r(C—N) = 1.15, r(C—C) = 1.50_5, ϕ(FCF) = 108.5°	(37)
$DC\equiv CD$	gas	IR	rotational constants	(38)
$CH_2=CH—CHO$	gas	MIW	rotational constants	(39)
$CH_2=C=CH_2$	gas	R	r(C=C) = 1.309	(40, 41)
$H—N=C=O$	crystal	XD	r(N—C) = 1.183, r(C—O) = 1.184	(42)
$HC\equiv C—CHO$	gas	MIW	rotational constants	(43)
$CH_3—C\equiv C—CH_3$	crystal	XD	r(C—C) = 1.45_7, r(C≡C) = 1.21_1	(44)
$CH_3—C\equiv C—Cl$	gas	MIW	The most reasonable set: r(C—Cl) = 1.6371, r(C≡C) = 1.2069, r(C—C) = 1.4584, r(C—H) = 1.117, ϕ(HCC) = 110° 46′, r(C—D) = 1.114, ϕ(OCC) = 110° 30′	(45)
$DC\equiv N$	gas	IR	rotational constants	(46)
$CH_3—C\equiv CH$	gas	MIW	The most reasonable set: r(CH) = 1.112 (Methyl), r(CD) = 1.108 (Methyl), r(C—C) = 1.458, r(C≡C) = 1.207, r(CH) = 1.060 (Acetylenic), r(CD) = 1.058 (Acetylenic), ϕ(HCH) = 108° 25′, ϕ(DCD) = 108° 32′, ϕ(HCC) = 110° 30′, ϕ(DCC) = 110° 23′	(47)
$CH_3—C\equiv N$	gas	ED	r(C—C) = 1.46_5, r(CN) = 1.15_5	(37)
$CH_3—C\equiv N$	gas	MIW	The most reasonable set: r(CH) = 1.112, r(CD) = 1.107, r(C—C) = 1.458, r(CN) = 1.157, ϕ(HCH) = 109° 16′, ϕ(HCC) = 109° 40′, ϕ(DCD) = 109°21′, ϕ (DCC) = 109° 35′	(47)
HCOOH	gas	MIW	The most reasonable set: r(CH) = 1.085, r(C=O) = 1.245, r(CO) = 1.312, r(OH) = 0.95, ϕ(OCO) = 124° 18′, ϕ(COH) = 107° 48′, ϕ(HCO) = 117° 51′	(48)
HCOF	gas	ED	r(CF) = 1.351, r(C=O) = 1.192, ϕ(OCF) = 121.9°	(49)
$HCONH_2$	gas	MIW	rotational constants (planarity)	(50)
Benzene	crystal	XD	r(C—C) = 1.39_2	(51)
Benzoic acid	crystal	XD	bond lengths and angles	(52)
Di-p-tolyl telluride	crystal	XD	r(C—Te) = 2.05, ϕ(C—Te—C) = 101°	(53)
Di-p-tolyl selenide	crystal	XD	r(C—Se) = 1.93, ϕ(C—Se—C) = 106°	(54)
Di-p-tolyl sulfide	crystal	XD	r(C—S) = 1.75, ϕ(C—S—C) = 109°	(55)
Fluorene	crystal	XD	bond lengths and angles	(56)
$C_5H_5—Fe—C_5H_5$	gas	ED	r(Fe—C) = 2.03, r(C—C) = 1.43, r(C—H=)1.09 (assumed)	(57)
s-Triazine $[—N=CH—]_3$	crystal	XD	r(C—N) = 1.319, r(CH) = 1.00, ϕ(N—C—N) = 126.8°, ϕ(CNC) = 113.2°	(58)
Parabanic acid $(CO)_2(NH)_2$	crystal	XD	bond lengths and angles	(59)

TABLE II (*continued*)

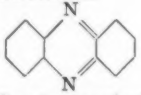
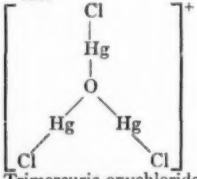
Molecule	State	Method	Bond lengths (Å) and angles	References
Cyanuric chloride	gas	ED	bond lengths and angles	(60)
Melamine	gas	ED	bond lengths and angles	
α-Phenazine 	crystal	XD	bond lengths and angles	(61)
Creatine monohydrate	crystal	XD	bond lengths and angles	(62)
Creatinine	crystal	XD	bond lengths and angles	(63)
Methyl guanidinium nitrate	crystal	XD	bond lengths and angles	(64)
1,3-Dimethyl-5-imino-tetrazol HCl (or HBr)	crystal	XD	Planarity of tetrazol ring: bond lengths and angles	(65)
Indanthrone	crystal	XD	bond lengths and angles	(66)
Codeine HBr	crystal	XD	bond lengths and angles	(67)
Vitamin B_{12} and related compounds	crystal	XD	bond lengths and angles	(68, 68a)
β-Caryophyllene alcohol chloride	crystal	XD	bond lengths and angles	(69)
Ethylene-palladium chloride	crystal	XD	bond lengths and angles	(70)
Styrene-palladium chloride	crystal	XD	bond lengths and angles	(71)
Urea	crystal	NMR	r(N—H) = 1.077	(72)
Glycine	crystal	NMR	r(N—H) = 1.074	(72)
Stearic acid	crystal	XD	bond lengths and angles	(73)
Glutamic acid	crystal	XD	bond lengths and angles	(74)
Tetradecan amide	crystal	XD	bond lengths and angles	(75)
Diacetylhexamethylene diamide	crystal	XD	bond lengths and angles	(76)
Polyisobutylene	solid	XD	r(CC) = 1.54 (assumed), ϕ(C—C—C) = 114°	(77)
Phenyl isocyanate dimer	crystal	XD	bond lengths and angles	(78)
Polycaproamide	solid	XD	bond lengths and angles	(79)
Silk fibroin	fiber	XD	bond lengths and angles	(80)
Tussah silk fibroin	fiber	XD	bond lengths and angles	(81)

TABLE II (*continued*)

Molecule	State	Method	Bond lengths (Å) and angles	References
SiD_3H	gas	IR	r(Si—H) = 1.4798	(82)
SiH_3I	gas	IR	r(Si—H) = 1.48 (assumed), r(SiI) = 2.45, (HSiH) = 109° 54′	(83)
Si_2Cl_6	gas	ED(S)	r(Si—Cl) = 2.01, r(Si—Si) = 2.24, ϕ(SiSiCl) = 109.5°	(23)
$[-Si(CH_3)_2-O-]_4$	crystal	XD	r(Si—O) = 1.65, r(Si—C) = 1.92, ϕ(Si—O—Si) = 142.5°, ϕ(O—Si—O) = 109°, ϕ(C—Si—C) = 106°	(84)
$[-Si(CH_3)_2-S-]_2$	gas	ED	bond lengths and angles	(85)
$[-Si(CH_3)_2-S-]_3$	gas	ED	bond lengths and angles	(85)
BF_4^-	crystal	NMR	r(B—F) = 1.43	(86)
B_2Cl_4	crystal	XD	r(B—Cl) = 1.72, r(B—B) = 1.80, ϕ(ClBCl) = 121.5°, ϕ(BBCl) = 119.1°	(87)
$NH_3^+-SO_3^-$	crystal	XD	r(S—N) = 1.75$_5$, r(S—O) = 1.43, 1.44, 1.45, ϕ(NSO) = 102, 102, 103°, ϕ(OSO) = 114, 115, 118°	(88)
CsI_3	crystal	XD	r(I—I) = 2.83, 3.03, ϕ(I-I-I) = 176.3°	(89)
SnI_4	crystal	XD	r(Sn—I) = 2.69	(89a)
$[-P(CH_3)_2-BH_2-]_3$			r(P—C) = 1.84, r(P—B) = 1.94, ϕ(CPC) = 100°, ϕ(BPB) = 118°, ϕ(BPC) = 109°, ϕ(PBP)112°, ϕ(HBH) = 119°	(90)
S_8	crystal	XD	r(S—S) = 2.037, ϕ(S—S—S) = 107° 48′	(91)
P_4S_7	crystal	XD	bond lengths and angles	(92)
P_4S_{10}	crystal	XD	bond lengths and angles	(92)
Hexafluorophosphoric acid	crystal	XD	r(P—F) = 1.73	(93)
AlN	crystal	XD	r(Al—N) = 1.917 or 1.885	(94)
Cupric tetra-amine sulfate	crystal	XD	bond lengths and angles	(95)
	crystal	XD	r(O—Hg) = 2.03, r(Hg—Cl) = 2.28	(96)
Trimercuric oxychloride $Hg(OHgCl)_2$	crystal	XD	r(Hg—O) = 2.16, r(Hg—Cl) = 2.66, etc.	(97)
Hg_2NHBr_2	crystal	XD	bond lengths and angles	(98)
HPO_4^{--}	crystal	XD	bond lengths and angles	(99)
$Na_{2-x}V_6O_{16}$	crystal	XD	bond lengths and angles	(100)

rotation through ca. $\pm 120°$ (124). One of the two *gauche* forms is the non-superposable mirror image of the other. Therefore, it will show optical activity, if it can be isolated by some means. So far no one has succeeded in this isolation in the case of a simple compound of the type $XH_2C—CH_2X$. However, if a ligand of this type is present in coordination complexes, it may exist in a single *gauche* form and consequently more optical isomers are possible than would be expected from the classical coordination chemistry in which such a ligand has been tacitly assumed to be in the *cis* form. Actually in 1,2-dithiocyanatoethane-dichloro-platinum (II), the $NCS \cdot H_2C—CH_2 \cdot SCN$ ligand has been shown to exist in the *gauche* form by spectroscopic method (129).

As mentioned above the stable angles of internal rotation in disubstituted ethanes are 0° and ca. $\pm 120°$. This is in general the case for all substituted ethanes, propanes, etc. This conclusion has been confirmed by recent measurements (130 to 140). For other substances similar results have been obtained (138, 141).

The energy difference between the rotational isomers depends to a considerable extent on the solvent. Usually in the solid state only one of the isomers is stable (124, 130, 131, 136, 142 to 147). In a few cases two forms are found in the solid state, e.g. $Br_2HC—CHBr_2$ (144, 145), and $IH_2C—CH_2—CH_2I$ (148).

The stable form in the solid state of the molecules of the types $XH_2C—CH_2X$ and $XH_2C—CH_2Y$ is the *trans* form (124, 131, 136), except for $ClH_2C—CH_2OH$ with internal hydrogen bonding (149) and $NC \cdot H_2C—CH_2 \cdot CN$ (150). In $Cl_2HC—CHCl_2$ (130) and $Br_2HC—CHBr_2$ (144) the *gauche* form was found to be stable in the solid state, although the latter substance crystallizes as *trans* molecules by employing a different method of cooling (145).

The determination of the energy difference between the rotational isomers has been continued (131, 138, 143, 147, 151). The results confirm previous conclusions (124).

Similar studies have been extended to other kind of substances (74, 141, 152) including amides (109, 124, 124a, 153). Furthermore, the calculation of stable internal rotation angles has been made for many amino acids and peptides (154). These results will help greatly towards determining the probable forms of a chain molecule, especially that of a polypeptide. Such a molecule will take various forms because of the internal rotation about single bonds. The calculation of chain forms of polymers, especially polypeptides, in terms of bond lengths, bond angles and internal rotation angles has been made (155, 156). As examples of recent experimental work concerning polymer chains, the structure determinations of polyglycine and polyethylene-glycol have been made by Crick & Rich (157) and by Davison (158), respectively.

So far, the equilibrium angles of internal rotation have been discussed.

This corresponds to the potential minimum of internal rotation. We are also interested in the information on the potential maximum, especially its height.

In ethane, $H_3C—CH_3$, the potential maxima correspond to three equivalent eclipsed forms and the height was found to be 2.875 kcal./mole according to Pitzer (159). It is interesting to note that the barrier height observed by Rubin, Levedahl & Yost (160) for $H_3C—CCl_3$ is nearly the same as for $H_3C—CH_3$, whereas those for both $H_3C—CH_2Cl$ (161) and $H_3C—CHCl_2$ (162) are much higher. In $H_3C—SiF_3$ the barrier height was estimated by Collins & Nielsen (163) as 1.44 kcal./mole. Extensive spectroscopic studies on fluorinated ethanes, including the barrier problem, are being continued by Nielsen and co-workers (164).

The 1 kcal./mole figure of Burkhard & Dennison (165) for the barrier height of CH_3OH against the much larger values previously obtained has been confirmed (18, 18a, 19, 166). For CH_3SH a lower value (0.7–0.8) kcal./mole) has been found (20, 21, 167). This is reasonable, since the CS distance is about 0.4 Å longer than the CO distance in CH_3OH. In CH_3NH_2 a barrier height of 1.9–2.0 kcal./mole has been found by thermal measurement by Aston & Gittler (168, 169) and microwave measurements by Shimoda *et al.* (170), Lide (171), and Nishikawa *et al.* (22). In $CH_3C{\equiv}CCH_3$ where the two rotating groups are separated far apart from each other, the spectroscopic data obtained by Mills & Thompson (172) are consistent with the assumption of unrestricted internal rotation of the methyl groups. The microwave spectrum of $CH_3—C{\equiv}C—CF_3$ observed by Lide & Kivelson (173) was also explained on the basis of a zero, or very low potential barrier. Aston & co-workers (174, 175) found a high potential barrier amounting to 5.3 kcal./mole for $ClF_2C—CF_3$ in which the interaction between the halogen atoms is considerable.

In most of the cases so far studied, the potential barrier can be explained as arising from the steric and electrostatic interactions between the rotating groups (124, 176). However, for the rotation about the O—O axis the dominant factor in determining the azimuth of one group relative to the other is the interaction of the two electronic clouds which are unsymmetrical about the O—O axis. For H_2O_2 containing this axis, the barrier height was estimated to be of the order of 4 kcal./mole (177). However, recent work tends to assign a much lower value (178, 179).

Another case of unsymmetrical electronic clouds about the axis of internal rotation is the one in which the axis partly acquires double bond character. For example, Lerner, Friend & Dailey (48) found the torsional frequency in HCOOH to be 667 cm^{-1} by microwave measurement. This corresponds to a considerably high barrier which is explained as being due to the large amount of double bond character of the C—O axis of internal rotation. In amides such is also the case as has been shown by nuclear magnetic resonance by Phillips (180) and infrared measurements (124, 181).

Palm & Kilpatrick (182) found a high barrier amounting to 9–10 kcal./mole for HNO_3.

As theoretical work in this field, the calculation of energy levels for internal rotation and over-all rotation of the CH_3BF_2 type molecules has been made by Wilson, Lin & Lide (183). Burkhard & Irvin (184) solved the wave equation for two asymmetric rigid molecules rotating about a common axis.

Transferability of Force Constants

It is well known that the vibrations of a complicated molecule may be treated conveniently by considering the group frequencies (185, 186). This shows that the force constants may be transferred from other molecules with similar structure. However, it should be noted that force constants have meaning only with respect to the specific model of the force field assumed for the calculation of normal vibrations.

Using the modified valence force field, Crawford & Brinkley (187) obtained transferable force constants for the molecules, CH_4, C_2H_6, C_2H_4, C_2H_2, HCN, CH_3CN, $CH_3C{\equiv}CH$ and $CH_3C{\equiv}CCH_3$ and the deuterium substituted molecules. Similar constants have since been calculated by several investigators for many methane derivatives (125). Jenkins (188) suggested that force constants vary with the inverse of the square of the equilibrium internuclear distance. Jones (188a) has found that a decrease in metal-oxygen bond distance is accompanied by a decrease in force constant in the crystalline sodium acetate complexes of U(VI), Np(VI), Pu(VI), and Am(VI).

From the viewpoint of the valence theory it is appealing to use a potential function containing the terms for bonded atoms and those corresponding to the repulsive force between non bonded atoms (119 to 123). Therefore, it would be interesting to discuss the transferability in terms of stretching, bending and repulsive force constants. In this case we have to take account of the intramolecular tension which arises from the atoms and electrons about a central atom, such as C and Si. The transferable force constants have been obtained from the normal vibration calculations of many molecules including methane and its halogen derivatives (119, 189), tetrahedral molecules (190), chlorobromo- and chloroiodosilanes (191), methylchlorosilanes (192), methylbromosilanes (193), ethylhalide, ethyl alcohol, dihalogenoethanes and ethylene chlorhydrin (194 to 198), hexachloroethane (119, 199), hexachlorodisilane (200), symtetrachloroethane (130), 1,1,1-trifluoroethane (201), polyethylene (119), n-paraffins (202, 203), cyclohexane (204), *trans*-1,4-dichlorocyclohexane (205), benzene (206), formaldehyde, phosgene and acetone (207, 208), acetaldehyde, formamide and formate ion (209, 210), chloroacetyl chloride and bromoacetyl chloride (211, 212), chloroacetone (142), diacetyl (213), guanidinium ion (214), and tetra-, tri-, and dihalogenoethylenes (215, 216).

By use of these constants, the normal frequencies of many molecules

containing a similar structure can be calculated within an error of five per cent. The values of these constants, therefore, help greatly towards making assignments of the observed infrared and Raman frequencies.

We have mentioned above that the transferability of the C—F bond length is not very satisfactory. This might have something to do with the value of the F · · · F repulsive constant which is much larger in magnitude than those of other atoms.

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